



AGRICULTURAL RESEARCH INSTITUTE

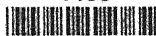
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JOURNALS FROM WHICH ABSTRACTS ARE MADE.

The following is a list of Journals from which abstracts are made (directly or indirectly) by the Chemical Society and the Society of Chemical Industry. The abbreviated titles printed in italics represent Journals abstracted by the Chemical Society, those printed in roman type being abstracted by the Society of Chemical Industry. Of the former Journals those indicated by an asterisk are also abstracted by the Society of Chemical Industry.

ABBREVIATED TITLE.	JOURNAL.
<i>Abh. Böhm. Akad.</i> . . .	Abhandlungen der Böhmischen Akademie.
<i>Abh. Deut. Naturwiss. Med. Ver. Böhmen.</i>	Abhandlungen der Deutschen Naturwissenschaftlichen und Medizinischen Verein, Böhmen.
<i>Acad. Sci. Fennicæ</i> . . .	Acta Societatis Scientiarum Fennicæ.
<i>Agric. Bull. F. M. S.</i> . . .	Agricultural Bulletin of the Federated Malay States.
<i>Agric. Exp. Stat. Univ. Wisconsin Res. Bull.</i>	Agricultural Experimental Station, University of Wisconsin, Research Bulletin.
<i>Agric. Gaz. S. Russia.</i> . . .	Agricultural Gazette of Southern Russia.
<i>Agric. J. India</i> . . .	Agricultural Journal of India.
<i>Agric. Ledger</i> . . .	Agricultural Ledger.
<i>Agric. Res. Inst., Pusa Rep. (Bull.)</i>	Agricultural Research Institute, Pusa, Report and Bulletins.
<i>Agric. and Sylvic</i> . . .	Agriculture and Sylviculture (Petrograd).
<i>Allgem. Brau.-Hopf. Zeit.</i> . . .	Allgemeine Brau- und Hopfen-Zeitung.
<i>Allgem. Gerber-Zeit.</i> . . .	Allgemeine Gerber-Zeitung.
<i>Allgem. Z. Bierbrau. u. Malzfabr.</i>	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
<i>Amat. Fotog.</i> . . .	Amateur Fotografen.
<i>Amer. Brewers' J.</i> . . .	American Brewers' Journal.
<i>Amer. Brewers' Rev.</i> . . .	American Brewers' Review.
<i>Amer. J. Bot.</i> . . .	American Journal of Botany.
<i>Amer. J. Dis. Children</i> . . .	American Journal of Diseases of Children.
<i>Amer. J. Pharm.</i> . . .	American Journal of Pharmacy.
<i>Amer. J. Physiol.</i> . . .	American Journal of Physiology.
<i>Amer. J. Publ. Health</i> . . .	American Journal of Public Health.
<i>*Amer. J. Sci.</i> . . .	American Journal of Science.
<i>Amer. Mach.</i> . . .	American Machinist.
<i>Amer. Min.</i> . . .	American Mineralogist.
<i>Amer. Perf.</i> . . .	American Perfumer.
<i>Amer. Phot.</i> . . .	American Photography.
<i>Anal. Fis. Quim.</i> . . .	Anales de la Sociedad Española Física y Química.
<i>Anal. Soc. Quim. Argentina</i>	Anales de la Sociedad Química Argentina.
<i>Analyst</i> . . .	Analyst.
<i>Annalen</i> . . .	Justus Liebig's Annalen der Chemie.
<i>Ann. Bot.</i> . . .	Annals of Botany.
<i>Ann. di Bot.</i> . . .	Annali di Botanica.
<i>Ann. Chim.</i> . . .	Annales de Chimie.
<i>Ann. Chim. Analyt.</i> . . .	Annales de Chimie Analytique.
<i>Annali Chim. Appl.</i> . . .	Annali di Chimica Applicata.
<i>Ann. Ecole Agric. Montpellier</i>	Annales de l'Ecole nationale d'Agriculture de Montpellier.
<i>Ann. Falsif.</i> . . .	Annales des Falsifications.
<i>Ann. Geol. Min. Russie</i>	Annuaire de la Géologie et des Mines de la Russie.
<i>Ann. hyg. pub. med. legale.</i>	Annales d'hygiène publique et de médecine légale.
<i>Ann. Inst. Mines, Petrograd</i>	Annales de l'Institut des Mines de Petrograd.
<i>Ann. Inst. Pasteur</i> . . .	Annales de l'Institut Pasteur.
<i>Ann. Inst. Polyt., Petrograd</i>	Annales de l'Institut Polytechnique de Petrograd.
<i>Ann. Physik</i> . . .	Annalen der Physik.
<i>Ann. Physique</i> . . .	Annales des Physique.
<i>Ann. R. Staz. Chim. Agrar. Sperim.</i>	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
<i>Ann. sci. Univ. Jassy</i> . . .	Annales scientifiques de l'Université de Jassy.

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ABBREVIATED TITLE.	JOURNAL.
<i>Ann. Soc. Geol. Belg.</i> ; <i>Publ. rel. au Congo Belge</i>	Annales de la Société géologique de Belgique: Publications relatives au Congo Belge.
<i>Apoth. Zeit.</i>	Apotheker-Zeitung.
<i>App. Sci.</i>	Applied Science.
<i>Arch. Gebi. Physik, Math. Chem.</i>	Arbeiten aus dem Gebiete der Physik, Mathematik und Chemie.
<i>Arch. Gesundh. Amt.</i>	Arbeiten aus dem Gesundheitsamte.
<i>Arch. Anat. Physiol.</i>	Archiv für Anatomie und Physiologie.
<i>Arch. Chem. Mikros.</i>	Archiv Chemie und Mikroskopie.
<i>Arch. Entw.-mech. Org.</i>	Archiv für Entwicklungsmechanik der Organismen.
<i>Arch. expt. Path. Pharm.</i>	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. farm. sper. sci. aff.</i>	Archivio di farmacologia sperimentale e scienze affini.
<i>Arch. Fisiol.</i>	Archivio di Fisiologia.
<i>Arch. Hyg.</i>	Archiv für Hygiene.
<i>Arch. Int. Med.</i>	The Archives of Internal Medicine.
<i>Arch. ital. Biol.</i>	Archives italiennes de Biologie.
<i>Arch. Med. Pharm. milit.</i>	Archives de Médecine et de Pharmacie militaires.
<i>Arch. Néerland.</i>	Archives Néerlandaises de sciences exactes et naturelles.
<i>Arch. Néerland. physiol.</i>	Archives Néerlandaises de physiologie de l'homme et des animaux.
<i>*Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Arch. physikal. Chem. Glas. Keram.</i>	Archiv für die physikalische Chemie der Glases und der Keramischen Massen.
<i>Arch. Sci. biol. Petrograd.</i>	Archives des Sciences biologiques, Petrograd.
<i>Arch. Sci. phys. nat.</i>	Archives des Sciences physiques et naturelles.
<i>Arch. Suikerind. Ned. Indie</i>	Archief voor de Suikerindustrie in Nederlandsch-Indië.
<i>Arkiv. Kem. Min. Geol.</i>	Arkiv. för Kemi, Mineralogi och Geologi.
<i>Arm. Beton.</i>	Armierter Beton.
<i>*Atti R. Accad. Lincei</i>	Atti della Reale Accademia dei Lincei.
<i>Atti R. Accad. Sci. Torino</i>	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Ist. Veneto Sci.</i>	Atti del Istituto Veneto di Scienze, Lettere ed Arti.
<i>Aust. Pharm. Notes</i>	Australian Pharmaceutical Notes and News.
<i>Beitr. Min. Japan</i>	Beiträge zur Mineralogie von Japan.
<i>Berg. Hüttenm. Rundsch.</i>	Berg- und Hüttenmannisches Rundschau.
<i>*Ber.</i>	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. bot. Ges.</i>	Berichte der Deutschen botanischen Gesellschaft.
<i>Ber. Deuts. pharm. Ges.</i>	Berichte der Deutschen pharmazeutischen Gesellschaft.
<i>Ber. Deut. physikal. Ges.</i>	Berichte der Deutschen physikalischen Gesellschaft.
<i>Ber. K. Sächs. Ges. Wiss.</i>	Berichte über die Verhandlungen der Königlich Sächsischen Gesellschaft der Wissenschaften.
<i>Ber. Oberhess. Ges. Natur. Heilkunde.</i>	Berichte der Oberhessischen Gesellschaft für Natur- und Heilkunde zu Giessen.
<i>Ber. Ohara Inst. landw. Forsch.</i>	Berichte des Ohara Instituts für landwirtschaftliche Forschungen.
<i>Berlin. Klin. Woch.</i>	Berliner Klinische Wochenschrift.
<i>*Bied. Zentr.</i>	Biedermann's Zentralblatt für Agrikulturchemie und rationalen Landwirtschafts-Betrieb.
<i>Biochem. Bull.</i>	Biochemical Bulletin.
<i>*Biochem. J.</i>	Biochemical Journal.
<i>*Biochem. Zeitsch.</i>	Biochemische Zeitschrift.
<i>Blätter Zucker.</i>	Blätter für Zuckerrübenbau.
<i>Bd. of Trade J.</i>	Board of Trade Journal.
<i>Bol. Acad. Nac. Ciencias, Córdoba.</i>	Boletín de la Academia Nacional de Ciencias, Córdoba.
<i>Boll. Chim. farm.</i>	Bolletino Chimico farmaceutico.
<i>Boll. Soc. Geol. Ital.</i>	Bolletino della Società Geologica Italiana.

ABBREVIATED TITLE.	JOURNAL.
<i>Boll. Soc. Med.-Chirurg.</i>	Bolletino della Società Medico-Chirurgica, Pavia.
<i>Bot. Centr.</i>	Botanisches Centralblatt.
<i>Bot. Gaz.</i>	Botanical Gazette.
<i>Brass. Malt.</i>	Brasserie et Malterie.
<i>Brau- u. Malzind.</i>	Brau- u. Malzindustrie.
<i>Braunkohle</i>	Braunkohle.
<i>Brewers' J.</i>	Brewers' Journal.
<i>Brit. and Col. Pharm.</i>	British and Colonial Pharmacist.
<i>Brit. J. Phot.</i>	British Journal of Photography.
<i>Brit. Med. J.</i>	British Medical Journal.
<i>Buletinul Chim.</i>	Buletinul Chimie.
<i>Bul. Soc. Romane Stiin.</i>	Buletinul Societatii Romane de Stiinte.
<i>Bull. Acad. roy. Belg.</i>	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Acad. Sci. Cracow</i>	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. Acad. Sci. Petrograd.</i>	Bulletin de l'Académie Impériale des Sciences de Petrograd.
<i>Bull. Acad. Sci. Roumaine</i>	Bulletin de la Section Scientifique de l'Académie Roumaine.
<i>Bull. Agric. Intell.</i>	Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases.
<i>Bull. Assoc. Chim. Suer.</i>	Bulletin de l'Association des Chimistes de Sucre et de Distillerie.
<i>Bull. Bureau of Standards (U.S.A.).</i>	Bulletin of the Bureau of Standards (U.S.A.).
<i>Bull. Com. Géol. Finlande.</i>	Bulletin de la Commission Géologique de Finlande.
<i>Bull. Dept. Agric. Ceylon.</i>	Bulletin of the Department of Agriculture, Ceylon.
<i>Bull. Dept. Agric. Trinidad</i>	Bulletin of the Department of Agriculture, Trinidad.
<i>Bull. Forest Exp. Stat. Meguro.</i>	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
<i>Bull. gén. Thérap.</i>	Bulletin général de Thérapieutique médicale, chirurgicale, obstétricale.
<i>Bull. Geol. Inst. Univ. Upsala.</i>	Bulletin of the Geological Institution of the University of Upsala.
<i>Bull. Geol. Soc. Amer.</i>	Bulletin of the Geological Society of America.
<i>Bull. Geol. Survey, U.S.A.</i>	Bulletin of the U.S. Geological Survey.
<i>Bull. Geol. Survey, West Australia.</i>	Bulletin of the Geological Survey, West Australia.
<i>Bull. Imp. Centr. Agric. Exp. Stat. Japan.</i>	Bulletin of the Imperial Central Agricultural Experimental Station of Japan.
<i>Bull. Imp. Inst.</i>	Imperial Institute Bulletin.
<i>Bull. Johns Hopkins Hospital</i>	Bulletin of Johns Hopkins Hospital.
<i>Bull. Ranade Indus. Econ. Inst. Poona.</i>	Bulletin of the Ranade Industrial and Economic Institute, Poona.
<i>Bull. School Mines and Met., Univ. Missouri</i>	Bulletin of the School of Mines and Metallurgy, University of Missouri.
<i>Bull. Sci. Pharmacol.</i>	Bulletin des Sciences Pharmacologiques.
<i>*Bull. Soc. chim.</i>	Bulletin de la Société chimique de France.
<i>*Bull. Soc. chim. Belg.</i>	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. chim. biol.</i>	Bulletin de la Société de chimie biologique.
<i>Bull. Soc. chim. Maurice</i>	Bulletin de la Société chimique de Maurice.
<i>Bull. Soc. d'Encour.</i>	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
<i>Bull. Soc. franç. Min.</i>	Bulletin de la Société française de Minéralogie.
<i>Bull. Soc. Franç. Phot.</i>	Bulletin de la Société Française de Photographie.
<i>Bull. Soc. Ind. Mulhouse</i>	Bulletin de la Société Industrielle de Mulhouse.
<i>Bull. Soc. Ind. Nord.</i>	Bulletin de la Société Industrielle du Nord de la France.
<i>Bull. Soc. Ind. Rouen</i>	Bulletin de la Société Industrielle de Rouen.

ABBREVIATED TITLE.	JOURNAL.
<i>Bull. Soc. Oural. Sci. Nat.</i>	Bulletin de la Société Ouralienne des Amateurs des Sciences Naturelles à Catherineberg.
<i>Bull. Soc. Pharm. Bordeaux</i>	Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
<i>Bull. Wellcome Trop. Res. Lab.</i>	Bulletin of the Wellcome Tropical Research Laboratory.
<i>Cairo Sci. J.</i>	Cairo Scientific Journal.
<i>Canada Dept. Mines Publ.</i>	Canada Department of Mines Publications.
<i>Canadian Med. Assoc. J.</i>	Canadian Medical Association Journal.
<i>Canadian Mining J.</i>	Canadian Mining Journal.
<i>Caoutchouc et Gutta-Percha</i>	Le Caoutchouc et le Gutta-Percha.
<i>Cement</i>	Cement.
<i>*Centr. Bakt. Par.</i>	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
<i>Centr. Kunstdüngerind.</i>	Centralblatt für Kunstdüngerindustrie.
<i>Centr. Min.</i>	Centralblatt für Mineralogie, Geologie und Palaeontologie.
<i>Centr. Zuckerind.</i>	Centralblatt für Zuckerindustrie.
<i>Céramique</i>	Céramique.
<i>Ch. of Comm. J.</i>	Chamber of Commerce Journal.
<i>Chem. App.</i>	Chemische Apparatur.
<i>Chem. Eng.</i>	Chemical Engineer.
<i>Chem. Erde</i>	Chemie der Erde.
<i>Chem. Ind.</i>	Chemische Industrie.
<i>*Chem. News</i>	Chemical News.
<i>Chem. Trade J.</i>	Chemical Trade Journal.
<i>Chem. Umschau Fett-Ind.</i>	Chemische Umschau über die Fett- und Harz-Industrie.
<i>*Chem. Weekblad</i>	Chemisch Weekblad.
<i>Chem.-Zeit.</i>	Chemiker-Zeitung.
<i>Chem. Zeitsch.</i>	Chemische Zeitschrift.
<i>*Chem. Zentr.</i>	Chemisches Zentralblatt.
<i>Chem. and Drug.</i>	Chemist and Druggist.
<i>Collegium</i>	Collegium.
<i>*Compt. rend.</i>	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Compt. rend. l'Acad. d'Agric.</i>	Comptes rendus des Séances de l'Académie d'Agriculture de France.
<i>Compt. rend. Soc. Biol.</i>	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
<i>Comptes rend. Trav. Lab. Carlsberg</i>	Comptes rendus des Travaux de Laboratoire de Carlsberg.
<i>Dept. Chem. S. Australia, Bull.</i>	Department of Chemistry, South Australia, Bulletins.
<i>Derm. Woch.</i>	Dermatologische Wochenschrift.
<i>Deut. Essigind.</i>	Deutsche Essigindustrie.
<i>Deut. Mechan. Zeit.</i>	Deutsche Mechaniker Zeitung.
<i>Deut. med. Woch.</i>	Deutsche medizinische Wochenschrift.
<i>Deut. Parfum. Zeit.</i>	Deutsche Parfumerie Zeitung.
<i>Deuts. Zuckerind.</i>	Deutsche Zuckerindustrie.
<i>Econ. Geol.</i>	Economic Geology.
<i>Econ. Proc. Roy. Dubl. Soc.</i>	Economic Proceedings of the Royal Dublin Society.
<i>Electrician</i>	Electrician.
<i>Elektrochem. Zeits.</i>	Elektrochemische Zeitschrift.
<i>Eng. and Min. J.</i>	Engineering and Mining Journal.
<i>Eng. News</i>	Engineering News.
<i>Eng. Rec.</i>	Engineering Record.
<i>Engrais</i>	L'Engrais.
<i>Exper. Stat. Rec.</i>	Experimental Station Record.
<i>Fachl. Mitt. Öst. Tabak.</i>	Fachliche Mitteilungen der Österreichische Tabakregie.
<i>Farber-Zeit.</i>	Färber-Zeitung.

ABBREVIATED TITLE.	JOURNAL.
Farben-Zeit.	Farben-Zeitung.
Farm	The Farm (Russia).
Fermentforsch.	Fermentforschung.
Ferrum	Ferrum.
Feuerungstechnik	Feuerungstechnik.
<i>Flora</i>	Flora.
<i>Földtani Közlöny</i>	Földtani Közlöny.
Fühlings Landw. Zeit.	Fühlings Landwirtschaftliche Zeitung.
Gas	Het Gas.
Gas J.	Gas Journal.
Gas Rec.	Gas Record.
* <i>Gazzetta</i>	Gazzetta chimica italiana.
<i>Geol. För. Förh.</i>	Geologiska Föreningens i Stockholm Förhandlingar.
<i>Geol. Mag.</i>	Geological Magazine.
Gerber	Gerber.
Gesundheitsing.	Gesundheitsingenieur.
Gornosaw. Djelo	Gornosawodskoje Djelo.
Gummi-Zeit.	Gummi-Zeitung.
<i>Handl. Vijft. Nat.</i>	Handelingen van het Vijftende Natuur.
Hawaii Agric. Exp. Stat. Bull.	Hawaii Agricultural Experiment Station Bulletins.
<i>Heart</i>	Heart.
Hess. Landw. Zeits.	Hessische Landwirthschaftliche Zeitschrift.
<i>Hyg. Rundsch.</i>	Hygienische Rundschau.
Indian Forest Bull.	Indian Forest Bulletin.
<i>Indian J. Med. Res.</i>	Indian Journal of Medical Research.
India-rubber J.	India-rubber Journal.
Ingenieur	De Ingenieur.
Int. Mitt. Bodenk.	Internationale Mittheilungen für Bodenkunde.
Int. Sugar J.	International Sugar Journal.
Int. Z. Metallog.	Internationale Zeitschrift für Metallographie.
<i>Int. Zeitsch. phys.-chem. Biol.</i>	Internationale Zeitschrift für physikalisch-chemische Biologie.
Iron Steel Inst. Carnegie Schol. Mem.	Iron and Steel Institute, Carnegie Scholarship Memoirs.
<i>Jahrb. K. K. Geol. Reichsanst.</i>	Jahrbuch der K. K. geologischen Reichsanstalt.
<i>Jahrb. Min.</i>	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
<i>Jahrb. Min. Beil.-Bd.</i>	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie, Beilage-Band.
<i>Jahrb. Radioaktiv. Elektr.</i>	Jahrbuch der Radioaktivität und Elektronik.
<i>Jahrb. wiss. Bot.</i>	Jahrbuch für wissenschaftliche Botanik.
<i>Jahresber. Ges. vaterl. Kultur.</i>	Jahresbericht der schlesischen Gesellschaft für vaterländische Kultur.
<i>Jernk. Ann.</i>	Jernkontorets Annaler.
J. d'Agric. prat.	Journal d'Agriculture Pratique.
* <i>J. Agric. Res.</i>	Journal of Agricultural Research.
<i>J. Agric. Sci.</i>	Journal of Agricultural Science.
J. d'Agric. Trop.	Journal d'Agriculture Tropicque.
J. Agric. Victoria	Journal of Agriculture, Victoria.
* <i>J. Amer. Chem. Soc.</i>	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association.
<i>J. Amer. Med. Assoc.</i>	Journal of the American Medical Association.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
* <i>J. Biol. Chem.</i>	Journal of Biological Chemistry, New York.
J. Board Agric.	Journal of the Board of Agriculture.

ABBREVIATED TITLE.	JOURNAL.
J. Canad. Min. Inst. . . .	Journal of the Canadian Mining Institute.
J. Chem. Ind. Tokyo . . .	See Kōgyō- Kwagaku-Zasshi.
J. Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
<i>J. Chim. physique</i> . . .	Journal de Chimie physique.
J. Coll. Agric. Sapporo . .	Journal of the College of Agriculture, Sapporo, Japan.
J. Coll. Agric. Tohoku . . .	Journal of the College of Agriculture, Tohoku Imperial University, Japan.
J. Coll. Agric. Tokyo . . .	Journal of the College of Agriculture, Tokyo Imperial University, Japan.
J. Coll. Eng. Univ. Tokyo	Journal of the College of Engineering, University of Tokyo.
* <i>J. Coll. Sci. Tokyo</i> . . .	Journal of the College of Science, Imperial University of Tokyo.
<i>J. Exp. Med.</i> . . .	Journal of Experimental Medicine.
J. Franklin Inst. . . .	Journal of the Franklin Institute.
J. Gasbeleucht. . . .	Journal für Gasbeleuchtung und Wasserversorgung.
<i>J. Genetics</i> . . .	Journal of Genetics.
<i>J. Geol.</i> . . .	Journal of Geology.
<i>J. Geol. Soc. Tokyo</i> . . .	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
<i>J. Hygiene</i> . . .	Journal of Hygiene.
J. Imp. Gas Assoc. Tokyo	Journal of the Imperial Gas Association of Tokyo.
J. Ind. Eng. Chem. . . .	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing . . .	Journal of the Institute of Brewing.
J. Inst. Petroleum Tech. . .	Journal of the Institute of Petroleum Technologists.
J. Inst. Sanit. Eng. . . .	Journal of the Institute of Sanitary Engineers.
J. Landw. . . .	Journal für Landwirtschaft.
J. Manchester School Tech.	Journal of the Manchester School of Technology.
<i>J. Marine Biol. Assoc. U.K.</i>	Journal of the Marine Biological Association of the United Kingdom.
<i>J. Med. Res.</i> . . .	Journal of Medical Research.
<i>J. Path. Bact.</i> . . .	Journal of Pathology and Bacteriology.
J. Pharm. Chim. . . .	Journal de Pharmacie et de Chimie.
<i>J. Pharm. Expt. Ther.</i> . .	Journal of Pharmacology and Experimental Therapeutics.
* <i>J. Physical Chem.</i> . . .	Journal of Physical Chemistry.
<i>J. Physiol.</i> . . .	Journal of Physiology.
<i>J. Physiol. Path. gén.</i> . . .	Journal de Physiologie et de Pathologie générale.
* <i>J. pr. Chem.</i> . . .	Journal für praktische Chemie.
<i>J. Proc. Asiatic Soc. Bengal.</i>	Journal and Proceedings of the Asiatic Society of Bengal.
J. Roy. Agric. Soc. . . .	Journal of the Royal Agricultural Society.
<i>J. Roy. Army Med. Corps</i> . .	Journal of the Royal Army Medical Corps.
J. Roy. Hort. Soc. . . .	Journal of the Royal Horticultural Society.
<i>J. Roy. Soc. New South Wales.</i>	Journal and Proceedings of the Royal Society of New South Wales.
<i>J. Roy. Soc. West Australia</i>	Journal of the Royal Society of West Australia.
* <i>J. Russ. Phys. Chem. Soc.</i>	Journal of the Physical and Chemical Society of Russia.
<i>J. Scot. Met. Soc.</i> . . .	Journal of the Scottish Meteorological Society.
J. Soc. Arts . . .	Journal of the Royal Society of Arts.
J. Soc. Dyers and Col. . . .	Journal of the Society of Dyers and Colourists.
J. Soc. Russe Métall. . . .	Journal de la Société Russe de Métallurgie.
J. Textile Inst. . . .	Journal of the Textile Institute.
J. Usines Gaz . . .	Journal des Usines à Gaz.
<i>J. Washington Acad. Sci.</i> . .	Journal of the Washington Academy of Science.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Steel Institute.
<i>K. Svenska Vet.-Akad. Handl.</i>	Kongliga Svenska Vetenskaps Akademiens Handlingar.

ABBREVIATED TITLE.	JOURNAL.
Kali	Kali.
Karbid u. Azet.	Karbid und Azetylen.
Kentucky Exp. Stat. Bull.	Kentucky Experimental Station, Bulletin.
Keram. Rundsch.	Keramisch Rundschau.
Kew Bull.	Kew Bulletin.
Kiserlet Közl.	Kiserlet Közlemények.
Klein u. Mittelbrauer . . .	Klein und Mittelbrauer.
Kongl. Landtbr. Handl. Tidskr.	See Bull. Agric. Intell.
Kögyö-Kwagaku-Zasshi (J. Chem. Ind. Japan).	Kögyö-Kwagaku-Zasshi (Journal of Chemical Industry, Japan).
* <i>Kolloid Zeitsch.</i>	Kolloid Zeitschrift.
* <i>Koll. Chem. Beihefte</i> . . .	Kolloid-chemische Beihefte.
<i>Kosmos</i>	Kosmos (Lemberg).
<i>Kühn-Archiv</i>	Kühn-Archiv.
Kunststoffe	Kunststoffe.
<i>Lancet</i>	The Lancet.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs.-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Leather Trades Rev.	Leather Trades Review.
Leather Trades Year Boo . .	Leather Trades Year Book.
Leather World	Leather World.
Ledertech. Rundsch.	Ledertechnische Rundschau.
Leipzig. Monatsch. Textil-Ind.	Leipziger Monatschrift für Textil-Industrie
<i>Le Radium</i>	Le Radium.
L'Ind. Chimica	L'Industria Chimica.
L'Ind. Chimique	L'Industrie Chimique.
Lilly Sci. Bull.	Lilly Scientific Bulletin.
Local Govt. Bd. Reports . .	Local Government Board Reports.
Louisiana Bull.	Louisiana Bulletin.
Louisiana Planter	Louisiana Planter.
Lunds. Univ. Årsskr.	Lunds Universitets Års-skrift.
<i>Math. és Termész. Ért.</i> . . .	Mathematikai és Természettudományi Értesítő, Budapest.
Mat. Grasses	Les Matières Grasses.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kongl. Vetenskapsakademiens Nobel-Institut.
Medd. on Grönland	Meddelser on Grönland.
Med. Chron.	Medical Chronicle.
Med. Klinik	Medizinische Klinik.
Mem. Acad. Sci. Petrograd.	Mémoires de l'Académie Impériale des Sciences de Petrograd.
Mem. Accad. Lincei	Memorie della Reale Accademia dei Lincei.
Mem. Accad. Sci. Torino . . .	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Kyōtō	Memoirs of the College of Science, Kyōtō Imperial University.
Mem. Coll. Sci. and Eng. Kyōtō Imp. Univ.	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Dept. Agric. India . . .	Memoirs of the Department of Agriculture in India.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mém. Poudres et Salpêtres . .	Mémoriale des Poudres et Salpêtres.
Mem. Soc. Ing. Civ.	Mémoires de la Société des Ingénieurs Civils de France.
Mem. Soc. Natur. Kiev	Mémoires de la Société des Naturalistes de Kiev.
Mem. Soc. Toscana Sci. Nat.	Memorie della Società Toscana di Scienze naturali residente in Pisa.
Metall u. Erz	Metall und Erz.
Met. and Chem. Eng.	Metallurgical and Chemical Engineering.
Metallurgie	Metallurgie.

ABBREVIATED TITLE.	JOURNAL.
Metrop. Water Bd. Rep.	Metropolitan Water Board Reports.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Min. and Eng. Rev.	Mining and Engineering Review.
Ministry of Agric. Egypt.	Ministry of Agriculture of Egypt. Technical Science Service.
Mitt. Centralst. wiss.-techn. Unters.	Mittheilungen aus der Centralstelle für wissenschaftlich-technische Untersuchungen.
Mitt. deut. Landw.-Ges.	Mittheilungen der deutschen Landwirthschafts-Gesellschaft.
Mitt. deut. milchwirt. Ver.	Mittheilungen des deutschen milchwirtschaftlichen Vereins.
Mitt. geol. Landesanst.	Mittheilungen der geologischen Landesanstalt von Elsass-Lothringen.
Mitt. k. Materialprüf.	Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt. k. k. Techn. Versuchsamt	Mittheilungen des k. k. Technischen Versuchsamtes.
Mitt. med. Ges. Tokyo	Mittheilungen der medizinischen Gesellschaft zu Tokyo.
Mitt. Naturforsch. Ges. Halle.	Mittheilungen der Naturforschenden Gesellschaft zu Halle.
Molk.-Zeit.	Molkerei-Zeitung.
*Monatsh.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Monatsh. Math. Physik	Monatshefte für Mathematik und Physik.
*Mon. Sci.	Moniteur Scientifique.
Montan. Rundsch.	Montanische Rundschau.
Month. Not. Roy. Astr. Soc.	Monthly Notices of the Royal Astronomical Society, London.
Münch. med. Woch.	Münchener medizinische Wochenschrift.
Mycol. Zentr.	Mycologisches Zentralblatt.
Nachr. Ges. Wiss. Göttingen.	Nachrichten von der Königlichen Gesellschaft der Wissenschaften zu Göttingen.
Nature	Nature.
Naturwiss.	Die Naturwissenschaften.
Naturw. Rundsch.	Naturwissenschaftliche Rundschau.
Nephthanoje Djelo	Nephthanoje Djelo.
New York Agr. Expt. Sta. Bull.	New York Agricultural Experiment Station Bulletins.
New Zealand Dominion Laby. Rept.	New Zealand Dominion Laboratory Reports.
Nova Acta Soc. Sci.	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
Nuovo Cim.	Il Nuovo Cimento.
Öfvers. Finska Vet.-Soc.	Öfversigt af Finska Vetenskaps-Societetens Förhandlingar, Helsingfors.
Oelmotor	Der Oelmotor.
Oesterr. Chem.-Zeit.	Oesterreichische Chemiker-Zeitung.
Oesterr. Z. Berg- u. Hüttenw.	Oesterreichische Zeitschrift für Berg- und Hüttenwesen.
Oil and Colour Trades J.	Oil and Colour Trades Journal.
Oil, Paint, and Drug Rep.	Oil, Paint, and Drug Reporter.
Översigt Danske Vid. Selsk.	Översigt over det Kongelige Danske Videnskabernes Selskab Forhandlingar.
Pahasapa Quart.	Pahasapa Quarterly.
Paper	Paper.
Paper Maker	Paper Maker.
Paper Making	Paper Making.
Papierfabr.	Papier-Fabrikant.
Papier-Zeit.	Papier-Zeitung.

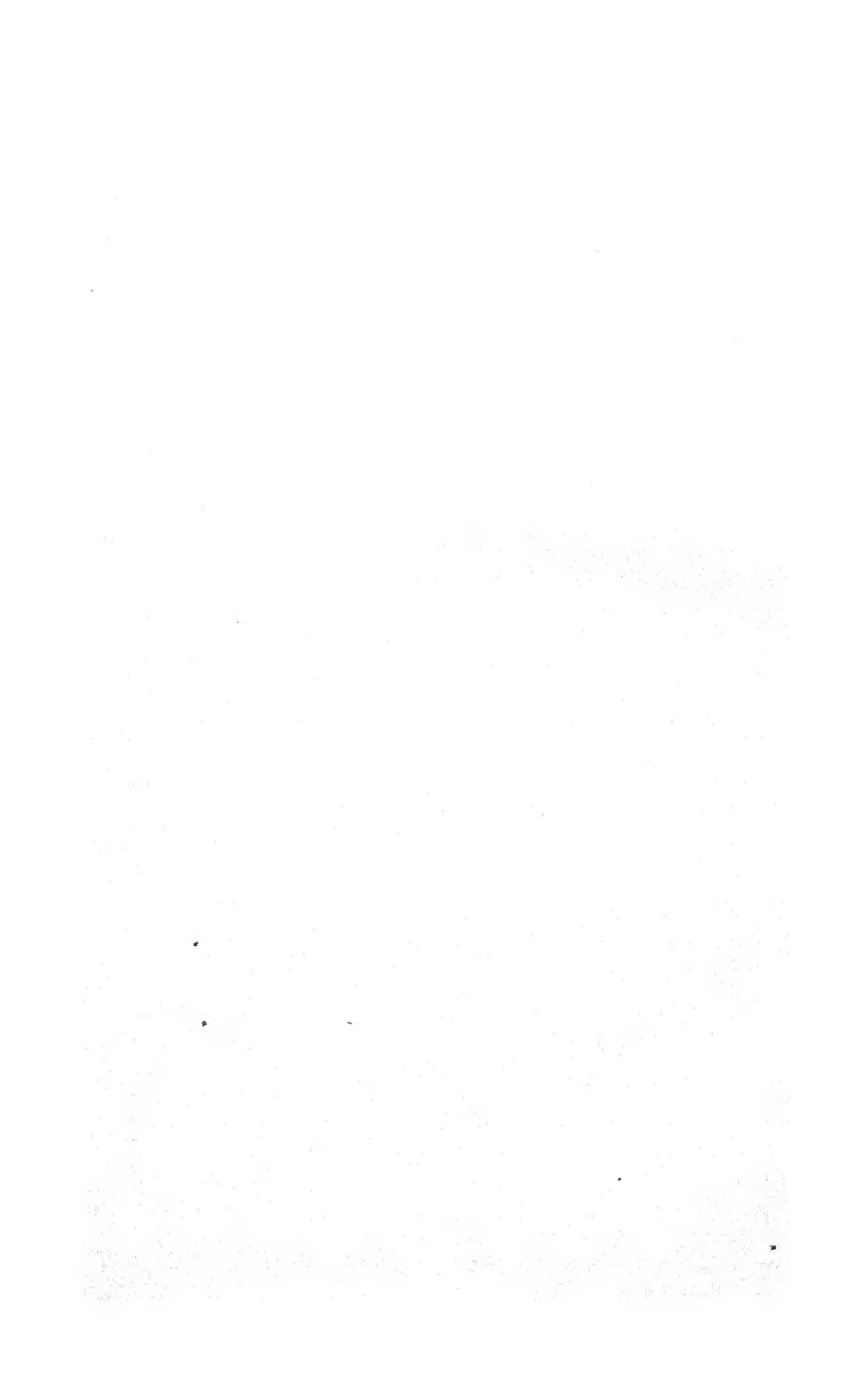
ABBREVIATED TITLE.	JOURNAL.
Perf. and Essent. Oil Rec. .	Perfumery and Essential Oil Record.
<i>Per. spis. Sofia</i> . . .	Periodicesko spisanie Sofia.
Petroleum . . .	Petroleum.
<i>Pflüger's Archiv</i> . . .	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. J. . . .	Pharmaceutical Journal.
Pharm. Post. . . .	Pharmazeutische Post.
Pharm. Weekblad . . .	Pharmaceutisch Weekblad.
Pharm. Zeit. . . .	Pharmazeutische Zeitung.
Pharm. Zentr.-h. . . .	Pharmazeutische Zentralhalle.
Pharmazert. J. . . .	Pharmazevtizski Journal.
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Elinburgh and Dublin).
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society of London.
Philippine J. Sci. . . .	Philippine Journal of Science.
Phot. Ind.	Photographische Industrie.
Phot. J.	Photographic Journal.
Phot. Korr.	Photographische Korrespondenz.
Phot. Rundsch. . . .	Photographische Rundschau.
<i>Physical Rev.</i>	Physical Review.
<i>Physikal. Zeitsch.</i> . .	Physikalische Zeitschrift.
Porto Rico Exper. Stat. Bull.	Porto Rico Experiment Station Bulletin.
<i>Proc. Amer. Phil. Soc.</i> .	Proceedings of the American Philosophical Society.
<i>Proc. Amer. Physiol. Soc.</i> .	Proceedings of the American Physiological Society.
* <i>Proc. Amer. Soc. Biol. Chem.</i>	Proceedings of the American Society of Biological Chemists.
Proc. Amer. Soc. Civ. Eng.	Proceedings of the American Society of Civil Engineers.
Proc. Amer. Soc. Testing Materials	Proceedings of American Society for Testing Materials.
Proc. Amer. Wood Preservers' Assoc.	Proceedings of American Wood Preservers' Association.
Proc. Austral. Inst. Min. Eng.	Proceedings of the Australasian Institute of Mining Engineers.
Proc. Brit. Foundrymen's Assoc.	Proceedings of British Foundrymen's Association.
<i>Proc. Camb. Phil. Soc.</i> .	Proceedings of the Cambridge Philosophical Society.
<i>Proc. Durham Phil. Soc.</i> .	Proceedings of the Durham Philosophical Society.
Proc. Eng. Soc. W. Pa. .	Proceedings of the Engineers' Society of Western Pennsylvania.
Proc. Inst. Civ. Eng. . .	Proceedings of the Institution of Civil Engineers.
Proc. Inst. Mech. Eng. .	Proceedings of the Institution of Mechanical Engineers.
Proc. Inst. Min. and Met. .	Proceedings of the Institution of Mining and Metallurgy.
* <i>Proc. K. Akad. Wetensch. Amsterdam.</i>	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
<i>Proc. Nat. Acad. Sci.</i> . .	Proceedings of the National Academy of Sciences.
<i>Proc. Nova Scotia Inst. Sci.</i>	Proceedings of the Nova Scotia Institute of Science.
<i>Proc. Phil. Soc. Glasgow</i> .	Proceedings of the Glasgow Philosophical Society.
<i>Proc. Physical Soc. London</i> .	Proceedings of the Physical Society of London.
<i>Proc. Physiol. Soc.</i> . . .	Proceedings of the Physiological Society.
<i>Proc. Roy. Irish Acad.</i> . .	Proceedings of the Royal Irish Academy.
* <i>Proc. Roy. Soc.</i>	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. Edin.</i> . .	Proceedings of the Royal Society of Edinburgh.
<i>Proc. Roy. Soc. Med.</i> . . .	Proceedings of the Royal Society of Medicine.
<i>Proc. Roy. Soc. Queensland</i> .	Proceedings of the Royal Society of Queensland.
<i>Proc. Roy. Soc. Tasmania</i> .	Proceedings of the Royal Society of Tasmania.
Proc. Soc. Chem. Ind. Victoria.	Proceedings of the Society of Chemical Industry, Victoria.

ABBREVIATED TITLE.	JOURNAL.
<i>Proc. Soc. Exp. Biol. Med.</i> .	Proceedings of the Society for Experimental Biology and Medicine.
<i>Proc. U.S. Nat. Mus.</i> .	Proceedings of the United States National Museum.
<i>Proc. verb. Soc. Toscana Sci. Nat.</i> .	Processi verbali Società Toscana di Scienze Naturali.
<i>Quart. J. Exp. Physiol.</i> .	Quarterly Journal of Experimental Physiology.
<i>Quart. J. Geol. Soc.</i> .	Quarterly Journal of the Geological Society.
<i>Quart. J. Med.</i> .	Quarterly Journal of Medicine.
<i>Queensland Agric. J.</i> .	Queensland Agricultural Journal.
<i>Radium in Biol. Heilkunde</i> .	Radium in Biologie und Heilkunde.
<i>Rec. Australian Mus.</i> .	Records of the Australian Museum.
<i>Rec. trav. bot. Néerland.</i> .	Recueil des travaux botaniques Néerlandaises.
<i>*Rec. trav. chim.</i> .	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Rend. Accad. Sci. Fis. Mat. Napoli.</i> .	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
<i>Rend. Ist. Lomb. Sci. Lett.</i> .	Rendiconti dell' Istituto Lombardo di Scienze e Lettere.
<i>Rend. Soc. Chim. Ital.</i> .	Rendiconto della Società Chimica Italiana.
<i>Rep. Aust. Assoc. Sci.</i> .	Report of the Australian Association for the Advancement of Science.
<i>Rep. Brit. Assoc.</i> .	Report of the British Association for the Advancement of Science.
<i>Rep. Pharm.</i> .	Repertoire de Pharmacie.
<i>Rev. Viticult.</i> .	Revista Viticult.
<i>Rev. gén. Bot.</i> .	Revue générale de Botanique.
<i>Rev. gén. Chim. pure appl.</i> .	Revue générale de Chimie pure et appliquée.
<i>Rev. Gén. Mat. Col.</i> .	Revue Générale des Matières Colorantes.
<i>Rev. Mét.</i> .	Revue de Métallurgie.
<i>Rev. Real Acad. Ciencias exact. Madrid.</i> .	Revista de la Real Academia de Ciencias exactas, Fisicas y Naturales de Madrid.
<i>Riv. Min. Crist. Ital.</i> .	Rivista di Mineralogia e Cristallografia Italiana.
<i>Russian Mining J.</i> .	Russian Mining Journal.
<i>Sbornik Klubu Pri.</i> .	Sbornik Klubu Prirodovedceho (Prague).
<i>Schimmel's Rep.</i> .	Schimmel's Reports.
<i>Schweiz. Apoth. Zeit.</i> .	Schweizerische Apotheker Zeitung.
<i>Schweiz. Woch. Chem. Pharm.</i> .	Schweizerische Wochenschrift für Chemie und Pharmacie.
<i>Science</i> .	Science.
<i>Scient. Amer.</i> .	Scientific American.
<i>*Sci. Ind. Rep. Roure-Bertrand Fils.</i> .	Scientific and Industrial Reports of Roure-Bertrand Fils.
<i>Sci. Proc. Roy. Dubl. Soc.</i> .	Scientific Proceedings of the Royal Dublin Society.
<i>Sci. Rep. Tohoku Imp. Univ.</i> .	Science Reports, Tohoku Imperial University.
<i>Sci. Trans. Roy. Dubl. Soc.</i> .	Scientific Transactions of the Royal Dublin Society.
<i>Seifenfabr.</i> .	Der Seifenfabrikant.
<i>Seifensied. Zeit.</i> .	Seifensieder Zeitung.
<i>Selsk. Khoz. Les. Petrograd</i> .	Selskoie Khoziaistvo i Lesovodstvo Petrograd.
<i>Shoe and Leather Rep.</i> .	Shoe and Leather Reporter.
<i>Silikat-Zeits.</i> .	Silikat-Zeitschrift.
<i>Sitzungsber. Ges. Naturwiss. Marburg.</i> .	Sitzungsberichte der Gesellschaft zur Beförderung der gesamten Naturwissenschaften in Marburg.
<i>Sitzungsber. Heidelberger Akad. Wis.</i> .	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
<i>Sitzungsber. K. Akad. Wiss. Berlin.</i> .	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
<i>Sitzungsber. K. Akad. München.</i> .	Sitzungsberichte der Königlich bayerischen Akademie der Wissenschaften zu München.
<i>Sitzungsber. K. Akad. Wiss. Wien.</i> .	Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Wien.
<i>Sitzungsber. Med. Naturwiss. Ges. Münster.</i> .	Sitzungsberichte der Medizinisch-Naturwissenschaftlichen Gesellschaft zu Münster-in-Westfalens.

ABBREVIATED TITLE.	JOURNAL.
<i>Sitzungsber. Naturforsch. Ges. Petrograd.</i>	Sitzungsberichte der Naturforschenden Gesellschaft zu Petrograd.
<i>Sitzungsber. Naturforsch. Ges. Rostock.</i>	Sitzungsberichte der Naturforschenden Gesellschaft zu Rostock.
<i>Sitzungsber. phys. med. Ges. Erlangen.</i>	Sitzungsberichte der physikalisch-medizinischen Gesellschaft zu Erlangen.
<i>Skand. Arch. Physiol.</i>	Skandinavisches Archiv für Physiologie.
<i>Smithsonian Miscell. Coll.</i>	Smithsonian Miscellaneous Collections.
<i>Soil Sci.</i>	Soil Science.
<i>South African J. Sci.</i>	South African Journal of Science.
<i>Spezialmonats. Brau- Malz.</i>	Spezialmonatshefte für Brau- und Malzerei betriebskontrolle.
<i>Sprechsaal.</i>	Sprechsaal.
<i>Stahl u. Eisen.</i>	Stahl und Eisen.
<i>Staz. sper. agr. ital.</i>	Stazioni sperimentali agrarie italiane.
<i>Strahlenther.</i>	Strahlentherapie.
<i>Sucr. Indig.</i>	Sucrerie Indigène.
<i>Süddeut. Apoth. Zeit.</i>	Süddeutsche Apotheker Zeitung.
<i>Suikerind.</i>	De Suikerindustrie.
<i>Suom. Tied. Toim.</i>	Suomalaisen Tiedeakatemia Toimituksia.
<i>Svensk Kem. Tidskr.</i>	Svenska Kemisk Tidskrift.
<i>T.</i>	Transactions of the Chemical Society.
<i>Teknikern.</i>	Teknikern.
<i>Tekn. Tidsk.</i>	Teknisk Tidskrift.
<i>Textile Col.</i>	Textile Colourist.
<i>Ther. Gegenw.</i>	Die Therapie der Gegenwart.
<i>Ther. Monatsh.</i>	Therapeutische Monatshefte.
<i>Tidsk. Kemi, Farm., Ter.</i>	Tidskrift Kemi, Farm. og Terape.
<i>Tidsk. Teknikern.</i>	Tidskriften Teknikern.
<i>Times Eng. Suppl.</i>	Times Engineering Supplement.
<i>Tonind.-Zeit.</i>	Tonindustrie-Zeitung.
<i>Trans. Amer. Ceram. Soc.</i>	Transactions of the American Ceramic Society.
<i>Trans. Amer. Electrochem. Soc.</i>	Transactions of the American Electrochemical Society.
<i>Trans. Amer. Foundrymen's Assoc.</i>	Transactions of the American Foundrymen's Association.
<i>Trans. Amer. Inst. Chem. Eng.</i>	Transactions of the American Institute of Chemical Engineers.
<i>Trans. Amer. Inst. Metals.</i>	Transactions of the American Institution of Metals.
<i>Trans. Amer. Inst. Min. Eng.</i>	Transactions of the American Institute of Mining Engineers.
<i>Trans. Engl. Ceram. Soc.</i>	Transactions of the English Ceramic Society.
<i>*Trans. Faraday Soc.</i>	Transactions of the Faraday Society.
<i>Trans. Inst. Metals.</i>	Transactions of the Institute of Metals.
<i>Trans. Iron and Steel Inst.</i>	Transactions of the Iron and Steel Institute.
<i>Tr. N. Eng. Inst. Min. and Met.</i>	Transactions of the North of England Institute of Mining and Metallurgy.
<i>Trans. New Zealand Inst.</i>	Transactions of the New Zealand Institute.
<i>Trans. Nova Scotia Inst. Sci.</i>	Transactions of the Nova Scotia Institute of Science.
<i>Trans. Path. Soc.</i>	Transactions of the Pathological Society.
<i>Trans. Roy. Irish Acad.</i>	Transactions of the Royal Irish Academy.
<i>Trans. Roy. Soc. Canada.</i>	Transactions of the Royal Society of Canada.
<i>Trans. Roy. Soc. Edin.</i>	Transactions of the Royal Society of Edinburgh.
<i>Trans. Surveyors' Inst.</i>	Transactions of the Surveyors' Institute.
<i>Trav. Mus. Geol. Acad. Sci. Petrograd.</i>	Travaux de Musée Géologique près l'Académie Impériale des Sciences de Petrograd.
<i>Trav. Soc. Natur. Petrograd.</i>	Travaux de la Société Impériale des Naturalistes de Petrograd.
<i>Tropenpflanzer.</i>	Tropenpflanzer.
<i>Tsch. Min. Mitt.</i>	Tschermak's Mineralogische Mitteilungen.

ABBREVIATED TITLE.	JOURNAL.
U.S. Bureau of Mines, Bull. and Tech. Papers.	United States Bureau of Mines, Bulletins and Technical Papers.
U.S. Bureau Plant Ind.	United States Bureau of Plant Industry.
U.S. Comm. Rept.	United States Commerce Reports, Daily Consular and Trade Reports.
U.S. Dept. Agric. Bull.	United States Department of Agriculture Bulletins.
U.S. Hyg. Labor. Bull.	United States Hygienic Laboratory Bulletins.
Univ. Illinois Bull.	University of Illinois Bulletins.
Utah Agric. Coll. Exper. Stat. Bull.	Utah Agricultural College Experiment Station Bulletins.
Ver. deut. Textilver.	Verein deutscher Textilveredlungsindustrie.
Verh. Geol. Reichsanst. Wien.	Verhandlungen der k. k. geologischen Reichsanstalt in Wien.
Verh. Ges. deut. Naturforsch. Aertze.	Verhandlung der Gesellschaft deutscher Naturforscher und Aertze.
Verh. Naturhist. med. Ver. Heidelberg.	Verhandlungen des naturhistorisch-medizinischen Vereins zu Heidelberg.
Verh. Naturhist. Rheinl.	Verhandlungen des naturhistorischen Vereins der preussischen Rheinlande und Westfalens.
Verh. Physiol. Ges. Berlin.	Verhandlungen der Physiologischen Gesellschaft zu Berlin.
Verh. Schweiz. Nat. Ges.	Verhandlungen der Schweizerischen Naturforschenden Gesellschaft, Basel.
Verslag Landb.	Verslag Landbouwkund Onderzoek Ryklandbouwproefstat.
Vet. Rec.	Veterinary Record.
Vict. Mem. Mus. Geol. Survey, Canada.	Victoria Memorial Museum Geological Survey of Canada, Bulletin
Videnskab. Skrifter	Skrifter udgivne af Videnskabsselskabet i Kristiania.
Wasser u. Gas	Wasser und Gas.
West Ind. Agric. News	West Indian Agricultural News.
West Ind. Bull.	West Indian Bulletin.
Westnik Sacch. Prom.	Westnik Saccharnoi Promyschlenosti.
Wiener Klin. Woch.	Wiener Klinische Wochenschrift.
Wiss. Abhandl. Physikal.-Tech. Reichsanst.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Wochbl. Papierfabr.	Wochenblatt für Papierfabrikation.
Woch. f. Brau.	Wochenschrift für Brauerei.
Yakugakuzashi	Yakugakuzashi.
Zeitsch. allg. Physiol.	Zeitschrift für allgemeine Physiologie.
*Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie.
*Zeitsch. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Zeitsch. Biol.	Zeitschrift für Biologie.
Zeitsch. deut. Geol. Ges.	Zeitschrift der deutschen Geologischen Gesellschaft.
*Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. exp. Path. Ther.	Zeitschrift für experimentelle Pathologie und Therapie.
Z. Farben-Ind.	Zeitschrift für Farben-Industrie.
Z. Forst- u. Jagdwesen	Zeitschrift für Forst- und Jagdwesen.
Z. Gärungsphysiol.	Zeitschrift für Gärungsphysiologie.
Z. ges. Brauw.	Zeitschrift für das gesammte Brauwesen.
Zeitsch. ges. exp. Med.	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Getreidew.	Zeitschrift für das gesamte Getreidewesen.
Z. ges. Schiess- u. Sprengstoffw.	Zeitschrift für das gesammte Schiess- und Sprengstoffwesen.
Zeitsch. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten.
Zeitsch. Immunit.	Zeitschrift für Immunitätsforschung und experimentelle Therapie.
Zeitsch. Instrument.	Zeitschrift für Instrumentenkunde.
Z. Kali	Zeitschrift für Kali.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.

ABBREVIATED TITLE.	JOURNAL.
Z. landw. Versuchsw. Oesterr.	Zeitschrift für das landwirtschaftlichen Versuchswesen in Oesterreich.
Z. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
* <i>Zeitsch. physikal. Chem.</i>	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physikal. Chem. Unterr.</i>	Zeitschrift für den physikalischen und Chemischen Unterricht.
<i>Zeitsch. physiol. Chem.</i>	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. prakt. Geol.</i>	Zeitschrift für praktische Geologie.
Z. Spiritusind.	Zeitschrift für Spiritusindustrie.
Z. Unters. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
<i>Zeitsch. wiss. Mikrosk.</i>	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
* <i>Zeitsch. wiss. Photochem.</i>	Zeitschrift für wissenschaftliche Photographie, Photo-physik und Photochemie.
Z. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.



JOURNAL OF THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Trimethylene [$\alpha\gamma$ -Propylene] Oxide. I. Preparation and Characterisation. C. G. DERICK and D. W. BISSELL (*J. Amer. Chem. Soc.*, 1916, **38**, 2478—2486).—The authors consider that the $\alpha\gamma$ -propylene oxide prepared and described by Reboul (A., 1879, 127) was very impure, and as the method of preparation only gave a 5% yield, they have devised a new method of preparing the oxide. γ -Chloropropyl acetate (75 grams) is added drop by drop to a mixture of potassium hydroxide (150 grams) and water (12 c.c.) at 100° with continual shaking. Along with $\alpha\gamma$ -propylene oxide some allyl alcohol and allyl chloride are obtained. These unsaturated compounds are removed from the crude distillate by the addition of bromine to the mixture immersed in ice, followed by subsequent distillation. The $\alpha\gamma$ -propylene oxide so obtained (yield, 22.5%) is a colourless, pleasant smelling, aromatic liquid, completely miscible with water, b. p. 47.8°/760 mm. (corr.), D_4^{25} 0.8930; n_D^{24} 1.3897. Bromine only attacks it very slowly, on long contact. A violent reaction occurs when phosphorus pentachloride is added to it, $\alpha\gamma$ -dichloropropane being formed. The oxide reacts with Grignard reagents to give the higher alcohols, hexan- α -ol being prepared in this way. With acetyl chloride, a vigorous action occurs, γ -chloropropyl acetate being regenerated. With ferric chloride solution, $\alpha\gamma$ -propylene oxide gives a brown precipitate.

W. G.

Esters of Telluric Acid. G. PELLINI (*Gazzetta*, 1916, **46**, ii, 247—250).—These esters cannot be prepared by the usual methods, but the *methyl* ester, $\text{Te}(\text{OMe})_6$, is readily obtained in white, shining laminae, m. p. 85—87° (corr., with previous softening), by gradual addition of finely powdered, dry telluric acid to a solution of diazomethane in absolute ether. It has a faint, irritant odour, which becomes more acute when its aqueous solution is heated, and it is readily hydrolysed by water, dilute hydrochloric acid, or dilute alkali hydroxide solution. The composition of this ester furnishes fresh confirmation of the constitution of telluric acid, $\text{Te}(\text{OH})_6$, and of the sexavalency of tellurium. T. H. P.

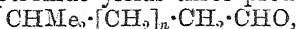
Manufacture of Esters. G. BOITEAU (Fr. Pat., 478435; from *J. Soc. Chem. Ind.*, 1916, **35**, 1131).—A mixture of an ester of ethylene glycol and an alcohol is heated, preferably in the presence of a small quantity of a catalyst, such as sulphuric acid. Acetaldehyde is evolved, and the corresponding ester of the alcohol is contained in the residue. The process is of general applicability, being obtained with primary, secondary, and tertiary alcohols and with aromatic hydroxy-compounds. H. W.

The Constitution of the Phosphoric Esters of Glycerol. O. BAILLY (*Ann. Chim.*, 1916, [ix], **6**, 96—154, 215—278).—A résumé of work already published (compare A., 1915, i, 73, 211, 371, 492; 1916, i, 113). W. G.

Preparation of Acetic Acid and Acetaldehyde from Acetylene. H. DREYFUS (Fr. Pat., 479656; from *J. Soc. Chem. Ind.*, 1916, **35**, 1179).—In the preparation of acetaldehyde by the combination of water with acetylene in the presence of a mercury salt, a liquid medium is employed in which the latter is soluble (for example, acetic acid) or which has a greater solvent power for acetylene than water (for example, acetone). In order to convert the acetaldehyde into acetic acid, oxidising substances are added, such as hydrogen peroxide, perborates, percarbonates, permanganates, dichromates, ozone, etc., or the oxidation may be effected by oxygen or air, with or without catalysts, such as cerium oxide, vanadium pentoxide, cerium salts, copper acetate, manganates, manganese or copper nitrate, platinum or palladium sponge, etc. Thus, acetylene (130 parts) and oxygen (80—100 parts) are passed into a mixture of glacial acetic acid (400 parts), water (100 parts), mercuric nitrate (50 parts), and cerium oxide (10 parts) at 50—100°. Acetic acid is produced continuously, and may be drawn off at intervals and distilled, the residue being returned to the reaction vessel. H. W.

Preparation of Anhydrides of Aliphatic Acids. H. DREYFUS (Fr. Pat., 478951; from *J. Soc. Chem. Ind.*, 1916, **35**, 1179).—Anhydrides of aliphatic acids may be prepared by distilling a dry, intimate mixture of a pyrosulphate with a salt of the appropriate acid; thus acetic anhydride is obtained from sodium acetate and sodium pyrosulphate. Diluents such as acetic anhydride or acetic acid may be employed. H. W.

Oxidation of Branched Chain Fatty Acids. I. Action of Hydrogen Peroxide on the Homologues of *iso*Butyric Acid. P. A. LEVENE and C. H. ALLEN (*J. Biol. Chem.*, 1916, 27, 433—462).—The oxidation of the higher homologues of *isobutyric* acid of the general formula $\text{CHMe}_2 \cdot [\text{CH}_2]_n \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ by means of hydrogen peroxide yields three products:



$\text{CHMe}_2 \cdot [\text{CH}_2]_n \cdot \text{COMe}$, and acetone. The reaction proceeds most favourably when the solution of the organic acid is slightly acid and when an amount of peroxide solution equivalent to $3\frac{1}{2}$ atoms of oxygen is employed for the reaction. Under these conditions, acetone is the predominating product and is identified by its *p*-nitrophenylhydrazine derivative. The aldehydes resulting from the oxidation in the α -position are identified by further oxidation to the corresponding acids.

The yield of acetone usually diminishes as the distance between the tertiary carbon atom and the carboxyl group becomes greater. A marked exception occurs in the case of *isovaleric* acid, which yields more acetone than *isobutyric* acid.

The acids required for the investigation are prepared according to the following set of reactions: $\text{R} \cdot \text{CH}_2 \cdot \text{OH} \rightarrow \text{R} \cdot \text{CH}_2\text{I} \rightarrow \text{R} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2 \rightarrow \text{R} \cdot \text{CH}(\text{CO}_2\text{H})_2 \rightarrow \text{R} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$. The higher acid thus obtained is converted into the corresponding alcohol, $\text{R} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \rightarrow \text{R} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} \rightarrow \text{R} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, which then forms the starting point for the preparation of the next higher homologous acid.

*iso*Amyl alcohol is purified by means of its barium compound, and the corresponding iodide, after condensation in the usual way with malonic ester, is transformed into δ -methylhexoic acid boiling at $216^\circ/762$ mm., which is rather higher than the values previously recorded. The ethyl ester has b. p. 182.7° (corr.)/750 mm., and the *amide*, $\text{C}_7\text{H}_{15}\text{ON}$, m. p. 103.5 — 104° (corr.). The reduction of the ester to the corresponding alcohol is effected by sodium, which is suspended in boiling toluene and divided into a fine emulsion by vigorous stirring. The yield of alcohol amounts to 60—65% of the theory, calculated on the basis of the ester used, or to 90—95% if the recovered acid is taken into consideration.

ϵ -Methylhexyl alcohol, $\text{C}_7\text{H}_{16}\text{O}$, has b. p. 170.5° (corr.)/755 mm., D_{25}^{25} 0.8192; *phenylurethane*, $\text{C}_{14}\text{H}_{21}\text{O}_2\text{N}$, m. p. 82.5° (corr.); *iodide*, b. p. 195 — 195.2° (corr.)/765 mm. By condensation of the iodide with malonic ester and subsequent hydrolysis, α -carboxy- ζ -methyl-octoic acid, $\text{C}_{10}\text{H}_{18}\text{O}_4$, is formed, m. p. 100 — 100.3° (corr.), *ethyl* ester, b. p. 155° (corr.)/15 mm., which is then converted into ζ -methyl-octoic acid, $\text{C}_9\text{H}_{18}\text{O}_2$, b. p. $248^\circ/765$ mm., or $140.5^\circ/15$ mm. (corr.); *amide*, m. p. 106.5° (corr.); *ethyl* ester, b. p. 220.5° (corr.)/764 mm. Subsequent treatment with sodium in the manner already indicated leads to the formation of η -methyl-octyl alcohol, b. p. 206° (corr.)/761 mm., D_{25}^{25} 0.8260; *phenylurethane*, m. p. 66.4° (corr.); *iodide*, b. p. 120° (corr.)/20 mm.

The following compounds have been similarly prepared: α -carb-*oxy- θ -methyldecoic acid*, $\text{C}_{12}\text{H}_{22}\text{O}_4$, m. p. 92° (corr.); *ethyl* ester,

b. p. 182° (corr.)/18 mm.; *θ-methyldecoic acid*, $C_{11}H_{22}O_2$, b. p. $174-174.5^{\circ}$ (corr.)/23 mm.

Starting from *isobutyl alcohol*, the corresponding compounds have been obtained with the following constants: *γ-methylpentioic acid*, b. p. $199.2-199.7^{\circ}$; *δ-methylamyl alcohol*, b. p. $153^{\circ}/760$ mm.; *phenylurethane*, m. p. 48° (corr.); *iodide*, b. p. 173.2° (corr.)/762 mm.; *α-carboxy-ε-methylheptioic acid*, $C_9H_{16}O_4$, m. p. 86.5° (corr.); *ε-methylheptioic acid*, $C_5H_{10}O_2$, b. p. $126-127^{\circ}$ (corr.)/14 mm. and 232° (corr.)/762 mm., *amide*, glistening plates, m. p. 114° (corr.), *ethyl ester*, b. p. 200.3° (corr.)/761 mm.; *ζ-methylheptyl alcohol*, b. p. 188.5° (corr.)/764 mm., $D_{25}^{20} 0.8230$, *phenylurethane*, m. p. $81-81.4^{\circ}$ (corr.), *iodide*, b. p. 100° (corr.)/17 mm.; *α-carboxy-η-methylnonoic acid*, m. p. $89.5-90^{\circ}$ (corr.); and *η-methylnonoic acid*, $C_{10}H_{20}O_2$, b. p. 155.6° (corr.)/16 mm.

After treatment of the above branched chain fatty acids with hydrogen peroxide, the presence of the higher ketones is demonstrated by an indirect method; the amount of the mixed ketones is estimated, and from this is deducted the amount of acetone present in the same solution. The higher ketones are not isolated in the pure condition.

H. W. B.

Lithofellic Acid. HANS FISCHER (*Ber.*, 1916, 49, 2413-2415. Compare A., 1915, i, 214).—Lithofellic acid changes into an oily lactone on treatment with hydrochloric acid and alcohol, and this yields *deoxylithofellenic acid*, $C_{20}H_{34}O_3$, m. p. $174-175^{\circ}$, on hydrolysis with barium hydroxide. The same lactone and unsaturated acid were described by Jünger and Klages (A., 1896, i, 194), but they gave the latter the formula $C_{15}H_{30}O_3$, and m. p. 152° .

A re-examination of lithofellic acid confirms the old formula, $C_{20}H_{36}O_4$. The author therefore abandons his idea that the acid is a hydrogenated cholic acid or a bile acid of any kind, and now believes that it originates in the fodder of the cattle, possibly in the pods of the South American *Prosopys*.

J. C. W.

Action of Oxalyl Chloride on Primary, Secondary, and Tertiary Alcohols. ROGER ADAMS and L. F. WEEKS (*J. Amer. Chem. Soc.*, 1916, 38, 2514-2519).—All the primary alcohols examined immediately reacted with oxalyl chloride at the ordinary temperature, giving simple esters (compare Staudinger, A., 1913, i, 604, 606). Three secondary alcohols were examined, and of these benzhydrol gave a small yield of benzhydryl ether, whilst phenylmethylcarbinol and menthol gave as principal products the corresponding unsaturated compounds, styrene and menthene. The three tertiary alcohols, trimethylcarbinol, dimethylethylcarbinol, and triphenylcarbinol, all yielded chlorides and oxalic acid, but pinacone yielded pinacolin and pinacone carbonate, the oxalyl chloride acting in this case like carbonyl chloride.

W. G.

The Crystallisation of Calcium Tartrate. F. D. CHATTAWAY (*J. Amer. Chem. Soc.*, 1916, 38, 2519-2522).—When a soluble

calcium salt is added to a neutral solution of a soluble tartrate, it is the *hexahydrate*, $C_4H_4O_6Ca \cdot 6H_2O$, which first separates in felted masses of needles. This form is, however, unstable at the ordinary temperature, and is transformed rapidly into the orthorhombic tetrahydrate. This change is facilitated by rise in temperature or by stirring the precipitate. W. G.

The Molecular Weight of some Alcoholates of Chloral and Butylchloral in Benzene Solution. MARGUERITE WILLCOX and ROGER F. BRUNEL (*J. Amer. Chem. Soc.*, 1916, **38**, 2533—2535).—A continuation of previous work (compare A., 1916, i, 710). The results obtained confirm the conclusions previously drawn, and show that the chloral- and butylchloral-alcoholates from primary alcohols are least highly dissociated, those of tertiary alcohols most highly dissociated, and those of secondary alcohols fall between them. W. G.

Manufacture of Acetals. A. T. KING and F. A. MASON (*Brit. Pat.*, 101428; from *J. Soc. Chem. Ind.*, 1916, **35**, 1131).—Acetals of the type $CH_3 \cdot CH(OR)_2$, in which R is an alkyl radicle, are obtained by treating a mixture of acetaldehyde (20—50%) and an aliphatic alcohol with hydrated or dehydrated chlorides or nitrates of aluminium, beryllium, calcium, cerium, lithium, magnesium, manganese, thorium, etc. with or without addition of hydrochloric or other acid. Thus a saturated solution of sodium chloride (20 c.c.) and aluminium chloride (10 grams) are added to 50 c.c. of a mixture containing 40% aldehyde and 60% alcohol, together with 1 c.c. of concentrated hydrochloric acid, and the mixture shaken for some time; the upper layer is washed with water and then with sodium carbonate solution, dried successively over calcium chloride and potassium carbonate, and finally fractionated to obtain the acetal. H. W.

Montan Wax. AD. GRÜN and E. ULBRICH (*Chem. Zentr.*, 1916, **2**, 402—403; from *Chem. Umschau Fett Harz-Ind.*, 1916, **23**, 57—60).—The authors are led to the conclusion that the unsaponifiable portion of Montan wax consists of montanone.

An amyl-alcoholic solution of the wax was neutralised with amyl-alcoholic sodium hydroxide and reduced with sodium powder; analyses of the product (acid number, 19.04; saponification number, 83.5; hydroxyl number, 30.5; esterification number, 64.8) pointed to the conclusion that an alcohol had been formed which had become esterified by the montanic acid. Hydrolysis of a solution of the product in xylene by means of alcoholic potassium hydroxide yielded *montanol*, $CH(C_{27}H_{55})_2 \cdot OH$, needles, m. p. 59—60°. The waxy, unsaponifiable portion of Montan wax, m. p. 59.6°, which does not contain an alcoholic hydroxyl group yielded montanol when reduced with sodium in amyl-alcoholic solution.

Montanic acid was converted into montanone according to the method of Easterfield and Taylor (*T.*, 1911, **99**, 2302); the ketone

had m. p. 59.6° (Easterfield and Taylor give 97°), and was identical with the unsaponifiable portion of the wax.

Montanyl acetate forms needles, m. p. 56.5° .

H. W.

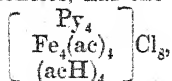
Iron-Acetylacetone-Pyridine Compounds. R. F. WEINLAND and EDMUND BÄSSLER (*Zeitsch. anorg. Chem.*, 1916, **96**, 109—138).—Ferri-acetylacetone dissolves in water to a red solution, becoming violet with acids. These violet solutions do not yield definite compounds. In presence of pyridine, however, crystalline compounds may be obtained. The chlorides may be prepared (1) by dissolving anhydrous ferric chloride in absolute alcohol and adding acetylacetone and pyridine, (2) by dissolving ferric acetate in absolute alcohol, adding alcoholic hydrogen chloride, acetylacetone, and pyridine; (3) by warming precipitated and partly dried ferric hydroxide with alcoholic hydrogen chloride and adding the same compounds; (4) by heating ferri-acetylacetone with alcoholic hydrogen chloride and pyridine. All the products are violet with black reflex, and are decomposed by water, yielding red solutions and precipitating ferric hydroxide. They are soluble in many organic solvents, including pyridine, to red solutions.

In order to determine whether a complex anion is present, the compounds have been mixed in alcoholic solution with lithium nitrate, bromide, iodide, and perchlorate, and with sodium platinichloride, but without result. The chlorine may, however, be replaced by the thiocyanate radicle by mixing with lithium, magnesium, or ammonium thiocyanate in alcoholic solution. The complex thiocyanates crystallise with a green reflex, and are very sparingly soluble. The composition of the products does not allow of definite conclusions as to the constitution of the acetylacetone compounds. Most of the compounds may be represented as containing a complex cation with four atoms of iron.

In the formulæ below, (ac) represents the acetylacetone residue, $\text{COMe}\cdot\text{CH}\cdot\text{CMe}\cdot\text{O}-$, Py represents pyridine, and in a single case (acac) represents the doubly enolised residue, $\text{CMe}\cdot\text{CH}\cdot\text{C}\cdot\text{CH}_2$.



The violet chloride, $\left[\text{Fe}_4\left(\frac{\text{Py}_5}{(\text{ac})_4}\right)\right]\text{Cl}_3$, may be obtained by either of the methods described above, by mixing the reagents in suitable proportion. A reddish-violet chloride, containing acetylacetone attached by subsidiary valencies, has the composition



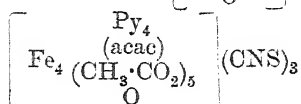
and when dissolved in a mixture of chloroform and benzene deposits yellowish-green crystals of a pyridine salt of a tetrachloro- or pentachloro-ferric acid, HFeCl_4 or H_2FeCl_5 .

Another reddish-violet chloride, $\left[\text{Fe}_5\left(\frac{\text{Py}_5}{(\text{acH})_3}\right)\right]\text{Cl}_3$, is prepared from the chloride solution. Tetrachlorides may also be obtained,

$\left[\text{Fe}_4 \begin{smallmatrix} \text{Py}_4 \\ (\text{ac})_8 \end{smallmatrix} \right] \text{Cl}_4$ being reddish-violet and $\left[\text{Fe}_4 \begin{smallmatrix} \text{Py}_3 \\ (\text{acH}) \end{smallmatrix} \right] \text{Cl}_4$ being red.

A red dichloride has the composition $\left[\text{Fe}_4 \begin{smallmatrix} \text{Py}_3 \\ (\text{ac})_9 \\ (\text{OH}) \end{smallmatrix} \right] \text{Cl}_2$.

The first-mentioned violet chloride yields with lithium thiocyanate, according to the proportions used, either $\left[\text{Fe}_4 \begin{smallmatrix} \text{Py}_3 \\ (\text{ac})_4 \end{smallmatrix} \right] \text{Cl}_4 (\text{CNS})_4$ or $\left[\text{Fe}_4 \begin{smallmatrix} \text{Py}_3 \\ (\text{ac})_4 \end{smallmatrix} \right] (\text{CNS})_8$. The reddish-violet octachloride or the red tetrachloride, in similar manner, yields $\left[\text{Fe}_4 \begin{smallmatrix} \text{Py}_4 \\ (\text{ac})_8 \end{smallmatrix} \right] (\text{CNS})_4$. By mixing ferric acetate and ammonium thiocyanate in acetylacetone and pyridine, the two compounds $\left[\text{Fe}_4 \begin{smallmatrix} \text{Py}_3 \\ (\text{ac})_8 \\ \text{O} \end{smallmatrix} \right] (\text{CNS})_2$ and



may be obtained.

C. H. D.

Composition of Commercial Glucose and its Digestibility. J. A. WESENER and G. L. TELLER (*J. Ind. Eng. Chem.*, 1916, **8**, 1009—1020).—Commercial glucose, or starch syrup, consists of a mixture of sugars and dextrans containing from 15 to 20% of water, about 0.06% of proteins, and a trace of mineral substances. The fermentable reducing sugars present are dextrose and maltose; two samples examined by the authors contained 11.7 and 17.2% of dextrose and 22.9 and 16.4% of maltose respectively. A third reducing substance, dextrin (or dextrans), is present, and this is not readily fermented by ordinary yeast, but may be made fermentable by the action of certain enzymes, especially those present in pancreatin, Takadiastase, and malt, as well as by the action of warm hydrochloric acid. The claim that glucose contains unfermentable reducing substances as reversion products, resulting from the action of acids on starch at high temperature, is untenable. Glucose consists, apparently, of substances which are wholly assimilable, and must be considered as a food having the nature of a sugar.

W. P. S.

Preparation of Bromoacetylglucose and certain other Bromoacetyl Sugars. J. K. DALE (*J. Amer. Chem. Soc.*, 1916, **38**, 2187—2188).—A saturated solution of hydrogen bromide in acetic anhydride was found to react directly with several sugars, and from the reaction mixture the bromoacetyl derivative could be isolated. By this method bromoacetylxylose, bromoacetylcellulose, bromoacetyllactose, and bromoacetylglucose were obtained in crystalline form with yields of 26, 60, 60, and 77% respectively. Bromoacetylmaltose was only obtained in the amorphous condition by this method.

W. G.

Nature of the Reducing Substances Precipitated by Basic Lead Acetate from Impure Sugar Solutions. H. PELLET (*Ann. Chim. anal.*, 1916, **21**, 217—223).—The precipitate produced when a molasses solution is treated with basic lead acetate contains a considerable quantity of a reducing substance. The latter consists of invert-sugar itself or a mixture of its constituent sugars; when the lead precipitate is separated and decomposed by sulphuric acid, the resulting solution is lævorotatory, the sugar it contains has the reducing power of invert-sugar, and is fermented completely by yeast. The reducing substance cannot be glucose, as stated recently by Davis (*J. Agric. Sci.*, 1916, **8**, 7), since this sugar is optically inactive and is not fermentable. If an invert-sugar solution is treated with equivalent quantities of basic lead acetate and sodium sulphate, the precipitate formed may contain up to 60% of the invert-sugar present, but the latter can be recovered by decomposing the precipitate with sulphuric acid. Normal lead acetate is recommended for the clarification of molasses solutions, calcium salts and excess of lead being removed from the solution before the copper-reducing power is estimated. W. P. S.

Volatile Organic Compounds, particularly Ethereal Oils, in the Manufacture of Sulphite Cellulose. ZOLTÁN KERTÉSZ (*Chem. Zeit.*, 1916, **40**, 945—948).—After reviewing the earlier investigations on the subject of the various volatile products formed in the commercial treatment of wood cellulose with alkali sulphite, the author describes the results of an examination of an ethereal, oily mixture, insoluble in water, obtained in this way from spruce. The oil, D_{20}^{25} 0.878, on distillation was found to consist mainly of cymene (approx. 80%), together with a sesquiterpene (10—12%), b. p. 136—138°/9 mm., $[\alpha]_D^{25}$ -12.7°, n_D^{25} 1.5124, D_{20}^{25} 0.9246, which gave a deep blue coloration with acetic anhydride and sulphuric acid (bromide, hydrogen haloids, and nitrosochlorides liquid), and a diterpene, D_{20}^{25} 0.9550, n_D^{25} 1.5254, $[\alpha]_D^{25}$ +4.9°, b. p. 180—190°/9 mm.; the higher boiling fractions also contained a small quantity of an amorphous, colourless solid, m. p. 67°, possibly a polyterpene. It is believed that these hydrocarbons are produced by the reducing action of the sulphite on the resins of the wood accompanied by polymerisation, isomerisation, and dehydration under the conditions of the treatment.

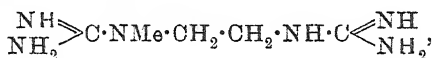
In addition to fermentation products, therefore, the following volatile substances have been observed as by-products in the sulphite treatment of cellulose: acetaldehyde, acetone, methyl and ethyl alcohols, formic and acetic acids, furfuraldehyde, cymene, a sesquiterpene, and a diterpene. D. F. T.

Lignoceric Acid from Rotten Oak Wood. M. X. SULLIVAN (*J. Ind. Eng. Chem.*, 1916, **8**, 1027—1028).—Rotten oak bark, when subjected to dry distillation, yielded a distillate consisting of tarry matter mixed with a white, crystalline solid; the latter was separated by crystallisation from alcohol, and then washed with cold alcohol and with light petroleum. The crystals thus

obtained were treated with lithium acetate in methyl alcohol solution; the precipitate which formed was separated, decomposed with sulphuric acid, and the liberated acid crystallised from alcohol; it had m. p. 80—82°, and was identified as lignoceric acid. A small portion of the lithium salt was soluble in methyl alcohol; this was isolated, and yielded an acid, m. p. 85°, which appeared to be inactive cerebronic acid (compare Levene and Jacobs, A., 1912, i, 936).
W. P. S.

Piperazine Cacodylate. ASTRUC (*Bull. Soc. chim.*, 1916, [iv], 19, 392—395).—When piperazine (1 mol.) is evaporated in aqueous solution with cacodylic acid (2 mols.) to a syrupy consistency, *piperazine cacodylate*, $[\text{AsOMe}_2(\text{OH})]_2 \cdot \text{C}_4\text{H}_{10}\text{N}_2 \cdot 4\text{H}_2\text{O}$, is obtained as colourless crystals, m. p. 54—55°, which on further heating become dry and decompose at 100°, giving off water and piperazine. In aqueous solution, it gives a white precipitate with mercuric chloride, a brown precipitate with iodine in potassium iodide, and yellow precipitates with picric acid or uranium acetate. The salt is acid to phenolphthalein and alkaline to helianthin-A.
W. G.

Amines. V. The Structure of Vitiatine. Synthesis of Methylethylenediamine. TREAT B. JOHNSON and GEORGE C. BAILEY (*J. Amer. Chem. Soc.*, 1916, 38, 2135—2145).—If the constitution assigned to vitiatine,



by Kutscher (compare A., 1907, ii, 562, 708) is correct, this substance should, on hydrolysis, yield ammonia and methylethylenediamine. With the view of elucidating this point, the authors have succeeded in preparing this latter base by the following series of actions.

Benzylsulphonamide, when boiled with alcoholic potassium hydroxide for half an hour, gave a *potassium* salt, which when mixed with bromoethylphthalimide in the dry state and heated for five hours at 100—110° yielded *phthalimidobenzylsulphone-ethylene-diamine*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{CH}_2\text{Ph}$, slender prisms, m. p. 175—176.5°. This substance when alkylated with methyl iodide in methyl-alcoholic solution in the presence of sodium gave *phthalimidobenzenesulphonemethylethylenediamine*, slender prisms, m. p. 177—178°, which when hydrolysed with an excess of concentrated hydrochloric acid at 120° for four hours yielded *methylethylenediamine hydrochloride*, colourless, micaceous flakes, m. p. 130—132°, giving a *platinichloride*, tabular prisms, m. p. 240—242° (decomp.), and a *picrate*, prisms, m. p. 220—222° (decomp.). The free amine distils slowly with steam. In the course of the work, a number of other derivatives of benzylsulphonamide were prepared and examined.

The potassium salt of benzylsulphonamide when heated with ethylene dibromide for five hours at 130° gave *dibenzylsulphone*.
b*

ethylenediamine, m. p. 202—204°, which with methyl iodide in the presence of alcoholic potassium hydroxide gave a mixture of *dibenzylsulphonedimethylethylenediamine*, m. p. 217—219°, and a very small amount of *dibenzylsulphonemethylethylenediamine*, m. p. 137°. The dimethyl derivative on hydrolysis with concentrated hydrochloric acid at 120—130° gave dimethylethylenediamine hydrochloride.

Bromoethylphthalimide when heated with the potassium salt of phenylsulphonamide for four hours at 100° gave *phthalimidophenylsulphone-ethylenediamine*, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} N \cdot CH_2 \cdot CH_2 \cdot NH \cdot SO_2Ph$, flat prisms, m. p. 175°.

By alkylation of benzyisulphonamide with the corresponding derivatives of benzyl chloride, the following compounds were prepared:

Benzylsulphondi-p-nitrobenzylamide, $CH_2Ph \cdot SO_2 \cdot N(CH_2 \cdot C_6H_4 \cdot NO_2)_2$, needles, m. p. 193—194°, and *benzylsulphon-p-nitrobenzylamide*, m. p. 182—183°.

Benzylsulphondi-o-nitrobenzylamide, prisms, m. p. 169—170°, and *benzylsulphon-o-nitrobenzylamide*, m. p. 124—126°.

Di-*p*-nitrobenzylamine hydrochloride and the corresponding ortho-compound were easily obtained by heating the corresponding sulphonamides with concentrated hydrochloric acid at 130—140°.

By the application of the method used by Johnson and Ambler for the synthesis of sarcosine (compare A., 1914, i, 264), the authors have prepared alanine. α -Bromopropionamide was digested in alcohol for six hours with the potassium salt of benzyisulphonamide, *benzylsulphonaminopropionamide*,

$CH_2Ph \cdot SO_2 \cdot NH \cdot CHMe \cdot CO \cdot NH_2$, prisms, m. p. 167°, was obtained, and on hydrolysis with a strong, boiling, aqueous solution of barium hydroxide yielded *benzylsulphonalanine*, $CH_2Ph \cdot SO_2 \cdot NH \cdot CHMe \cdot CO_2H$, plates, m. p. 164—165°, which when heated with hydrochloric acid for two hours at 130° gave alanine hydrochloride. W. G.

The Pyrogenetic Decomposition of Amides. I. R. S. BOEHNER and C. E. ANDREWS (*J. Amer. Chem. Soc.*, 1916, **38**, 2503—2505).—Acid amides may be decomposed into the cyanides and water by heating them in a flask with substances such as aluminium oxide, pumice stone, or glass, the flask being provided with an outlet sufficiently high up to permit the volatile cyanide to distil off, while the amides condense and drop back on the hot contact material. Using aluminium oxide, the best proportions are 50 grams of oxide and 10 grams of amide, the temperature of the bath being about 250—260°, but varying with the amide. The time required is about four hours, and the yields obtainable vary from 54% in the case of benzamide to 72% in the case of hexoamide. Formamide under these conditions distilled off practically unchanged, and phenylacetamide sublimed over too readily. W. G.

The Pyrogenetic Decomposition of Amides. II. R. S. BOEHNER and A. L. WARD (*J. Amer. Chem. Soc.*, 1916, **38**, 2505—2507. Compare preceding abstract).—In this case the amides were passed in the form of vapour over the contact material heated in a tube, using a current of air to aid the passage of the amide. The most satisfactory temperature was found to be 425°, and the contact materials, placed in order of efficiency, were: pumice stone, sand, aluminium oxide, and graphite. In this case the decomposition was practically theoretical. W. G.

The Constitution of Carbamides. III. The Reaction of Urea and of Thiourea with Acetic Anhydride. Potassium Thiourea. EMIL ALPHONSE WERNER (T., 1916, **109**, 1120—1130. Compare T., 1915, **107**, 715; 1914, **105**, 924, etc.).—When urea is heated with acetic anhydride, the yield of acetylurea is poor, on account of the decomposition of the greater part of the urea with formation of acetamide and diacetamide, only that part of the urea which has undergone isomerisation to the form



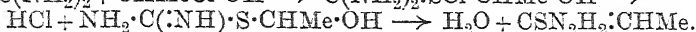
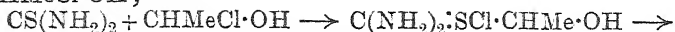
becoming acetylated (compare T., 1913, **103**, 1014, 2281). The addition of sulphuric acid favours the production of this form from the cyclic form, $\text{NH}\cdot\text{C}\begin{smallmatrix} \text{NH}_3 \\ \diagup \text{O} \end{smallmatrix}$, which the author believes to

represent the normal constitution of urea, and in the presence of a little sulphuric acid acetylurea can be obtained in a yield approaching 80% of the theoretical. Although urea cannot be converted into diacetylurea in one operation, acetylurea in the presence of sulphuric acid can be acetylated to diacetylurea of the probable constitution NH:C(OAc)NHAc (compare Kohmann, A., 1915, i, 944). Thiourea on treatment with acetic anhydride yields both the acetyl and the diacetyl derivative (compare Kohmann, *loc. cit.*), the formula given for the latter being analogous to that for the oxygen analogue, whilst the monoacetyl compound is regarded as an equilibrium mixture of the two forms, $\text{C}(\text{:NH})\begin{smallmatrix} \diagup \\ \text{S} \end{smallmatrix} \text{---} \text{NH}_2\text{Ac}$ and

NH:C(SH)NHAc . Potassium ethoxide and thiourea in the presence of alcohol react with formation of a compound, $\text{CSN}_2\text{H}_3\text{K(CSN}_2\text{H}_4)_2$, needles, m. p. 145°. For experimental details see the original. D. F. T.

The Interaction of Aldehydes and Thiocarbamides in the Presence of Acids. AUGUSTUS EDWARD DIXON and JOHN TAYLOR (T., 1916, **109**, 1244—1262).—In acidic aqueous solution thiocarbamide reacts with acetaldehyde, giving a deposit of a substance of the composition $\text{CSN}_2\text{H}_5\text{:CHMe}$, due to the spontaneous decomposition of an intermediate unstable isothiocarbamide base, $\text{NH}_2\cdot\text{C}(\text{:NH})\cdot\text{S}\cdot\text{CHMe}\cdot\text{OH}$, the “hydrochloride” of which, $\text{C}_3\text{H}_5\text{ON}_2\text{S}\cdot\text{HCl}$, is producible by the interaction of thiocarbamide and α -chloroethyl alcohol, and also of acetaldehyde and thiocarbamide hydrochloride. The insoluble reaction product from thiocarbamide and acetaldehyde may also be accompanied by a sub-

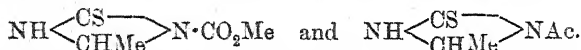
stance, $\text{CSN}_2\text{H}_2\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{O}$. The series of changes giving rise to the main product is probably as follows: $\text{CHMe}\cdot\text{O} + \text{HCl} \rightarrow \text{CHMeCl}\cdot\text{OH}$;



The composition assumed for the intermediate unstable base is confirmed by that of the somewhat more stable *ethoxyethyl iminothiocarbamate*, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{S}\cdot\text{CHMe}\cdot\text{OEt}$, the *hydrochloride* of which is produced on treating an alcoholic solution of acetaldehyde containing thiocarbamide in suspension with hydrogen chloride.

The behaviour of formaldehyde towards thiocarbamide resembles that of acetaldehyde, the product being a colourless, subcrystalline substance, $\text{CSN}_2\text{H}_2\cdot\text{CH}_2$, produced by dehydration of the intermediate base, which is even less stable than the corresponding acetaldehyde derivative. The action of hydrogen chloride on thiocarbamide in aqueous formaldehyde yields a syrupy substance, $\text{CSN}_2\text{H}_4\cdot\text{CH}_2\text{O}\cdot\text{HCl}$, which on neutralisation gave a substance, $\text{CSN}_2\text{H}_2\cdot\text{CH}_2$, formed by the dehydration of the unstable base corresponding with the salt; the *picrate*, $\text{C}_2\text{H}_6\text{ON}_2\text{S}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, analogous to the hydrochloride, is obtainable by the addition of formaldehyde to thiocarbamide in saturated picric acid solution.

Alkyl and aryl substituted thiocarbamides, when treated with hydrogen chloride in the presence of formaldehyde or acetaldehyde, likewise yield syrupy "*hydrochlorides*" of the same type as those derived from thiocarbamide itself; when their solutions are neutralised, the mono- and di-substitution derivatives give the corresponding bases and condensation products, whilst the tri- and tetra-substitution derivatives are unable to form condensation products. From acyl substituted thiocarbamides syrupy "*hydrochlorides*" are obtainable in a similar manner, but on account of the ease with which the bases undergo hydrolysis it was not found possible to prepare from them the corresponding condensation products; these, however, can be produced by the interaction of the acylthiocarbimides with aldehyde-ammonia in the presence of acetone, the compounds obtained from carbethoxythiocarbimide, carbomethoxythiocarbimide, and acetylthiocarbimide respectively according in composition with the formulæ $\text{NH}\langle\begin{smallmatrix}\text{CS} \\ \text{CHMe}\end{smallmatrix}\rangle\text{N}\cdot\text{CO}_2\text{Et}$,



Methylene iodide and thiocarbamide in hot alcohol react readily with formation of an *isothiocarbamide base*, $\text{CH}_2[\text{S}\cdot\text{C}(\text{NH})\cdot\text{NH}_2]_2$.

The constitution of the above "*hydrochlorides*," bases, and condensation products is discussed, together with the probable mechanism of the reactions observed in the formation and decomposition of the first-named.

Other compounds, such as benzaldehyde, salicylaldehyde, cinnamaldehyde, and certain ketones show evidence of condensation with thiocarbamide. For experimental details the original should be consulted.

D. F. T.

The Preparation of Nitriles. II. The Preparation of Aliphatic Nitriles. G. D. VAN EPPS and E. EMMET REID (*J. Amer. Chem. Soc.*, 1916, **38**, 2120—2128).—The method of preparing aromatic nitriles by heating the zinc salt of the acid with lead thiocyanates (compare A., 1910, i, 169) has been extended to the preparation of aliphatic nitriles. In addition, other metallic thiocyanates were used, and the results compared with those of lead thiocyanate. A wide range of metallic acetates was also tried in place of zinc acetate. Taking all the results into consideration, the best method is to use the zinc salt of the acid and lead thiocyanate in the proportion of one to two by weight. In the case of acetone nitrile, the crude distillate is best purified by mixing it with half its volume of water, saturating it with solid potassium carbonate or ammonia gas, separating the top layer, and fractionating it. An excellent yield of acetone nitrile is obtained by using cuprous thiocyanate in place of the lead salt. The yields are better with the acids of high molecular weight than with acetic acid, and a much larger yield is obtained from hydrocinnamic acid than from cinnamic acid. W. G.

The Preparation of Nitriles. III. The Catalytic Preparation of Nitriles. G. D. VAN EPPS and E. EMMET REID (*J. Amer. Chem. Soc.*, 1916, **38**, 2128—2135).—Acetone nitrile may be prepared by passing acetic acid vapour, mixed with a moderate excess of ammonia, over alumina or thoria at 500°, the yield reaching as much as 85%. The yield is variable, and depends on the activity of the catalyst and the velocity of the gases. The results show that 500° is the optimum temperature, and that alumina is a better catalyst than thoria. The presence of water in the acetic acid causes a diminution in the yield. When the acetic acid was replaced by acetone or ethyl acetate, no nitrile was obtained, and acetic anhydride gave lower yields than the acid itself. W. G.

Reactions under High Pressures. IV. Synthesis of Cyanides in the Electric Autoclave. ARTHUR STÄHLER (*Ber.*, 1916, **49**, 2292—2294).—In an earlier paper (A., 1913, ii, 697) the author described the production of boron nitrides by heating together boron trioxide and carbon in an atmosphere of nitrogen, in a special furnace capable of withstanding temperatures up to 2500° and pressures up to 500 atmospheres. The analogous production of cyanides has now been investigated.

Sodium and potassium carbonates when heated with carbon and nitrogen under 60 atm. pressure are converted to the extent of 95% into cyanides. Lithium cyanide may also be prepared in this way. The alkaline-earth carbonates mainly yield cyanamide under ordinary pressures, but only cyanides if the pressures are great. Magnesium, glucinum, and aluminium oxides give neither cyanides nor nitrides under these conditions. J. C. W.

Action of Sulphur on Naphthenes under Pressure. WALTER FRIEDMANN (*Chem. Zentr.*, 1916, ii, 485—486; from *Petroleum*, 1916, **11**, 978—982. Compare *Chem. Zentr.*, 1916, i, 1285).—Markovnikov and Spady have shown that when octa-

naphthene is heated with sulphur at 220—230° and the product subjected to nitration, trinitro-*m*-xylene is produced, and that during the first reaction small quantities of high-boiling products containing sulphur are also formed. The present investigation has been undertaken with the object of elucidating the mechanism of the transformation of naphthenes into aromatic hydrocarbons. *cyclo*Hexane has been heated under pressure with sulphur, and the product fractionated under diminished pressure. By nitration of the fractions of lowest boiling point, *m*-dinitrobenzene has been isolated; from the intermediate fraction, b. p. 40—60°/vacuum, thiophenol has been obtained, whilst the residue contains phenyl sulphide. Benzene cannot be identified among the products of the reaction, and it is probably not formed as an intermediate product. Without doubt the sulphur removes hydrogen, but the action only proceeds as far as dihydrobenzene, which is simultaneously oxidised and nitrated by the nitrating acid. The degradation of *cyclo*hexane to *cyclo*hexadiene is represented by the scheme: $C_6H_{12} + S = C_6H_{11} \cdot SH$; $C_6H_{11} \cdot SH - H_2S \rightarrow C_6H_{10}$ (*cyclo*hexene); $C_6H_{10} + S + H_2S \rightarrow C_6H_{10}S_2$; $C_6H_{10}S_2 - 2H_2S \rightarrow C_6H_8$ (*cyclo*hexadiene); $C_6H_8 + 2S + 2H_2S = C_6H_{10}S_4$; $C_6H_{10}S_4 - 3H_2S = C_6H_5 \cdot SH$.

Methyl*cyclo*hexane has been similarly heated with sulphur and the product fractionated. The portions, b. p. 100.5—120°, yield trinitrotoluene, m. p. 82°, on nitration; thiocresol was isolated from the fraction, b. p. 80—130°/11 mm.

The different fractions obtained by distillation of the product of the interaction of sulphur and octanaphthene (1:3-dimethyl*cyclo*hexane) react more or less strongly with bromine or permanganate. The portions, b. p. 30—90°/11 mm., yield trinitro-*m*-xylene, m. p. 181—182°, when nitrated; when the fraction, b. p. 90—100°/11 mm., is distilled at the ordinary pressure, thiol-*m*-xyleneol, b. p. 210—215°, is obtained (the *mercury* salt, $[C_8H_9S_2]_2Hg$, crystallises in needles). The yield of thioxylenol is small; this is explained by the fact that it is accompanied by 3:3'-dimethyldibenzyl, which can be isolated by repeated fractionation of the portion, b. p. 110—180°/12 mm. This hydrocarbon is actually obtained when *m*-xylene is heated under pressure with sulphur, but it has not been proved if it can be obtained from a 1:3-dimethyl*cyclo*hexadiene. It appears, therefore, probable that octanaphthene is in part converted into xylene as intermediate product when heated with sulphur. Genetic relationships between the aromatic and hydroaromatic hydrocarbons of petroleum are not known, and it is scarcely possible to account for the presence of both classes of substance in oils.

H. W.

Preparation of Benzene, Toluene, and other Aromatic Hydrocarbons from Petroleum and other Hydrocarbons.

W. F. RITTMANN (Brit. Pat., 1915, 9163; from *J. Soc. Chem. Ind.*, 1916, 35, 1103).—Hydrocarbon oils are subjected to a temperature at which sudden gasification occurs and, whilst in the gaseous condition, are cracked at a temperature not less than 600°, preferably

650—800°, and at a pressure not less than 4.2 kilos. per sq. cm., preferably 17.6 kilos. per sq. cm. H. W.

Treatment of Xylene and other Aromatic Hydrocarbons to obtain Lower Hydrocarbons of the Same Series. SYNTHETIC HYDRO-CARBON Co. (Fr. Pat., 479786; from *J. Soc. Chem. Ind.*, 1916, **35**, 1103).—Xylene or other hydrocarbon is subjected, in form of a vapour, to a temperature not below 400° and a pressure not exceeding 14 kilos. per sq. cm. With higher temperatures (600—850°) a lower pressure, capable of being reduced to half an atmosphere, may be used. Under the latter conditions, 30% of toluene has been produced from xylene. H. W.

Preparation of Chloro-derivatives of Organic Substances. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Fr. Pat., 479645; from *J. Soc. Chem. Ind.*, 1916, **35**, 1131).—The substance to be chlorinated is heated with manganese dioxide and hydrochloric acid or with manganese dioxide, sulphuric acid, and a metallic chloride. For example, a mixture of benzene (200 kilos.), manganese dioxide (100 kilos.), and concentrated hydrochloric acid (400 kilos.) is heated at a temperature a little lower than the boiling point of benzene. H. W.

Halogenation. XIV. Bromination of Hydrocarbons by means of Bromine and Nitric Acid. RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE (*J. Amer. Chem. Soc.*, 1916, **38**, 2545—2552).—Bromination, like chlorination (compare A., 1915, i, 114), can be carried out by using a mixture of nitric and hydrobromic acids, but it is preferable to use a mixture of bromine and nitric acid. All the bromine enters the molecule, the nitric acid helping the oxidation of hydrogen bromide to bromine as soon as it is formed. Brominations are effected very rapidly and energetically. The method is specially suitable for moderately light hydrocarbons, the process not being so satisfactory with the higher ones, owing to the possibilities of nitration taking place.

With the calculated quantities of bromine and nitric acid acting for a short time, benzene yields bromobenzene, whereas if an excess of bromine and acid acts for a long time, the chief product is *p*-dibromobenzene. Toluene gives a mixture of *o*-bromotoluene and 3:4-dibromotoluene if the time allowed is short, and penta-bromotoluene if an excess of bromine and nitric acid acts for a long time. *o*-Xylene yields respectively bromo-*o*-xylene and tetrabromo-*o*-xylene with *o*- and *p*-toluic acids; *m*-xylene yields respectively a mixture of bromo- and dibromo-*m*-xylenes and tetrabromo-*xylene*, and *p*-xylene yields a mixture of bromo- and dibromo-*p*-xylenes, and tetrabromo-*p*-xylene with *p*-toluic acid, according as the time allowed for the action is short or long. Similarly, mesitylene yields respectively bromomesitylene and tribromomesitylene. On short bromination, ethylbenzene gives a mixture of *o*- and *p*-bromoethylbenzenes. W. G.

Mononitrohalogenobenzenes with Mobile Halogen. W. BORSCHÉ, L. STACKMANN, and J. MAKAROFF-SEMLJANSKI (*Ber.*, 1916, **49**, 2222—2243).—The reactivity towards sodioacetoacetic and

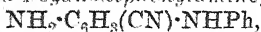
sodiummalonic esters of the halogen in the three pairs of compounds 4-bromo-3-nitrobenzonitrile and 5-bromo-2-nitro-*p*-toluonitrile, 4-bromo-3-nitroacetophenone and 2-chloro-5-nitro-4-methylacetophenone, and 4-bromo-3-nitro- and 2-bromo-5-nitro-benzophenones has been investigated. It is found, as usual, that the nitro-group confers greatest mobility on the halogen atom if it is adjacent to it, and that the activating influence of the cyano, acetyl, and benzoyl groups, whether ortho or para to the halogen, falls rapidly in the order given. The first and third compounds are easily obtained, and so other reactions have been studied with them.

One nitro-group is not sufficient to render a halogen atom active towards ethyl sodiomalonate, *o*-bromonitrobenzene, for example, being unaffected.

4-Bromo-3-nitrobenzonitrile is readily obtained by adding *p*-bromobenzonitrile to ice-cold fuming nitric acid. This reacts with an ethereal suspension of methyl sodiomalonate to form *methyl 2-nitro-4-cyanophenylmalonate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{CN}) \cdot \text{CH}(\text{CO}_2\text{Me})_2$, in white leaflets, m. p. 129.5° , which is converted by boiling with a mixture of acetic acid and some 60% sulphuric acid into *2-nitro-4-carboxyphenylacetic acid*, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$. This melts at 222° and changes into 2-nitro-*p*-toluic acid, and forms a *methyl ester*, in white leaflets, m. p. 76.5° . The above malonate, and also *methyl 2:4-dinitrophenylmalonate*, silvery leaflets, m. p. 95° , are stable towards ammonia.

Ethyl sodioacetoacetate reacts much more sluggishly than the malonate, but yields *ethyl 2-nitro-4-cyanophenylacetoacetate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{CN}) \cdot \text{CHAc} \cdot \text{CO}_2\text{Et}$, in stout, yellow needles, m. p. 85° . If gaseous ammonia is led into an ethereal solution of this, acetamide is deposited, and *ethyl 2-nitro-4-cyanophenylacetate*, pale yellow, glistening needles, m. p. 96° , is left in the solution. The ketone hydrolysis of the acetoacetate is achieved by boiling it with acetic acid and a little 60% sulphuric acid, whereby the cyano-group is also affected. *2-Nitro-4-carboxybenzyl methyl ketone* [*3-nitro-4-acetonylbenzoic acid*] forms long needles, m. p. 151.5° , and yields a *methyl ester*, in leaflets, m. p. 88.5° . The latter gives an orange-coloured *phenylhydrazone*, m. p. 116° , and reacts with benzenediazonium chloride in the presence of sodium acetate to form *α -phenylhydrazido-2-nitro-4-carbomethoxybenzyl methyl ketone*, $\text{CO}_2\text{Me} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CAc} : \text{N} \cdot \text{NHPh}$, in orange-coloured needles, decomp. 185° .

4-Bromo-3-nitrobenzonitrile reacts very readily with aniline in the presence of sodium acetate to form 2-nitro-4-cyanodiphenylamine. This may be reduced by means of tin and alcoholic hydrochloric acid to 2-amino-4-cyanodiphenylamine,

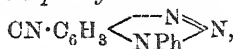


m. p. 154° , which reacts with acetic anhydride and sodium acetate to form 5-cyano-1-phenyl-2-methylbenziminazole,



needles, m. p. 179° , and with nitrous acid to give 5-cyano-1-phenyl-

aziminobenzene [9-cyano-1-phenylbenzo-1:2:3-triazole],



colourless needles, m. p. 186°.

Piperidine reacts with the bromonitrobenzonitrile in the same way, giving 3-nitro-4-piperidinobenzonitrile, in brilliant, orange-coloured, stout needles, m. p. 110—111°, and this is readily hydrolysed by the above mixture of acetic and sulphuric acids to 3-nitro-4-piperidinobenzoic acid, yellow needles, m. p. 202—203° (decomp.). The nitrile is reduced by a cold solution of stannous chloride to 3-amino-4-piperidinobenzonitrile, m. p. 68—69°, b. p. 203—204°/16 mm., but tin and hydrochloric acid produce 6-chloro-3-amino-4-piperidinobenzonitrile, in white needles, m. p. 78—79°.

The bromonitrobenzonitrile also reacts with ammonia if heated with an alcoholic solution at 100°, and yields 3-nitro-4-aminobenzonitrile, in yellow needles, m. p. 159—160°. This may be hydrolysed as above to 3-nitro-4-aminobenzoic acid, or reduced to 4-cyano-o-phenylenediamine, m. p. 145—146°, which condenses with benzil to form 6-cyano-2:3-diphenylquinoxaline, $\text{CN} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{N}:\text{CPh} \\ | \\ \text{N}:\text{CPh} \end{array}$, m. p. 179—180°.

4-Bromo-3-nitrobenzonitrile differs from bromo-2:4-dinitrobenzene in its behaviour towards phenylhydrazine and potassium xanthate. With the former agent it gives a compound, $\text{C}_{26}\text{H}_{16}\text{ON}_8$, m. p. 168—169°, instead of the expected substance of the formula $\text{CN} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{N} \\ | \\ \text{N} \end{array} \text{NPh}$, and with the latter it yields di-2-nitro-4-cyano-phenyl disulphide, $(\text{CN} \cdot \text{C}_6\text{H}_3 \cdot \text{NO}_2)_2\text{S}_2$, as a yellow powder, instead of a monosulphide.

5-Bromo-2-nitro-*p*-toluonitrile is conveniently obtained by nitrating the bromo-*p*-toluonitrile. The bromine atom in it is not very reactive, for methyl sodiomalonate gives only a very small yield of methyl 6-nitro-4-cyano-*m*-tolylmalonate,

$\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me}(\text{CN}) \cdot \text{CH}(\text{CO}_2\text{Me})_2$,
as pale yellow, silky needles, m. p. 91°.

p-Bromoacetophenone is readily converted into 4-bromo-3-nitroacetophenone, m. p. 116·5°, by mixing a solution in concentrated sulphuric acid at -5° with fuming nitric acid. This reacts with methyl sodiomalonate to form methyl 2-nitro-4-acetylphenylmalonate, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Ac} \cdot \text{CH}(\text{CO}_2\text{Me})_2$, in stout, pale brown rhombohedra, m. p. 96°, and with aniline and anhydrous sodium acetate to give 2-nitro-4-acetyldiphenylamine, in orange-red, rhombic leaflets, m. p. 108—109°. This may be reduced by means of a boiling solution of stannous chloride in a mixture of acetic and hydrochloric acids to 2-amino-4-acetyldiphenylamine, pale yellow leaflets, m. p. 165—166°, which reacts with nitrous acid to form 5-acetyl-1-phenylaziminobenzene [5-acetyl-1-phenyl-1:2:3-benzotriazole, $\text{C}_6\text{H}_3\text{Ac} \begin{array}{c} \text{N}:\text{N} \\ | \\ \text{NPh} \end{array}$, m. p. 199—200°. This compound forms

a sparingly soluble oxime, m. p. 222°, which is transformed by

phosphorus pentachloride into a *substance*, $C_{14}H_{11}ON_4Cl$, m. p. 265—267°.

4-Bromo-3-nitroacetophenone also reacts with piperidine to give 3-nitro-4-piperidinoacetophenone, in orange-red crystals, m. p. 90·5—91·5° (*oxime*, red needles, m. p. 122—123°), and with phenylhydrazine to yield merely the *phenylhydrazone*, $C_{14}H_{12}O_2N_3Br$, in red needles, m. p. 144—146°.

3-Chloro-*p*-tolyl methyl ketone is obtained from *m*-chlorotoluene and acetyl chloride as an oil, b. p. 127°/17 mm., which forms a *semicarbazone*, leaflets, decomp. 192—194°, and may be oxidised by alkaline permanganate to *o*-chloroterephthalic acid. When nitrated in sulphuric acid solution at -12° it yields 3:6-chloro-nitro-*p*-tolyl methyl ketone, in pale yellow needles, m. p. 75—76°, and this forms a *semicarbazone*, decomp. 215—217°, and a *phenylhydrazone*, slender, red needles, m. p. 127—129°. The nitrated ketone reacts with ethyl sodiomalonate to give ethyl 5-nitro-4-acetyl-*m*-tolylmalonate, $NO_2 \cdot C_6H_4MeAc \cdot CH(CO_2Et)_2$, in pale yellow leaflets, m. p. 65—66°, with aniline to form *phenyl*-6-nitro-4-acetyl-*m*-tolylamine, $NO_2 \cdot C_6H_4MeAc \cdot NHPh$, in slender, dark yellow needles, m. p. 135·5—136°, and with piperidine to yield 6-nitro-3-piperidino-*p*-tolyl methyl ketone, in long, orange-red prisms, m. p. 85°. The above nitrated diphenylamine may be reduced by tin and hydrochloric acid to *phenyl*-2-amino-4-acetyl-*m*-tolylamine, pale yellow leaflets, m. p. 112°, which forms an *acetyl* compound, $NHAc \cdot C_6H_4MeAc \cdot NHPh$, m. p. 78—80°.

4-Bromo-3-nitrobenzophenone, m. p. 124°, reacts very sluggishly with methyl sodiomalonate, and the isomeric 2-bromo-5-nitro-compound to no appreciable extent. The crude methyl 2-nitro-4-benzoylphenylmalonate is a dark brown, viscous oil, which may be hydrolysed by boiling with a mixture of acetic and sulphuric acids to form 2-nitro-4-benzoylphenylacetic acid, in white leaflets, m. p. 142°.

J. C. W.

Aromatic Nitro-derivatives. VI. General Considerations. M. GIUA (*Gazzetta*, 1916, **46**, ii, 256—272. Compare A., 1916, i, 205).—The author discusses the results obtained in his five previous papers on the influence of nitro-groups in an aromatic nucleus on the replaceability of other groups present, reference being made to Laubenheimer's rule and to Koerner's rule. The various structures which have been suggested for the benzene ring are also discussed.

T. H. P.

Nitration of Toluene to Trinitrotoluene. IRWIN W. HUMPHREY (*J. Ind. Eng. Chem.*, 1916, **8**, 998—999).—In the manufacture of trinitrotoluene it is generally preferred to make crude mononitrotoluene by nitrating toluene with a mixture of sulphuric acid (D 1·84) and nitric acid (D 1·42), and then to nitrate the mononitrotoluene to trinitrotoluene by treatment with more concentrated acids. In the latter part of the process, the best yields are obtained by operating at a temperature somewhat below 140°, using 98% sulphuric acid and concentrated nitric acid (D 1·52),

and maintaining the final nitrating mixture at 120—125° for two and a-half hours. The proportion of acids and toluene should be such that the water content of the final mixture is about 4.4%.

W. P. S.

Mixtures of Nitrated Explosives. II. M. GIUA (*Gazzetta*, 1916, 46, ii, 272—277. Compare A., 1915, i, 950).—The system picric acid-2:4:6-trinitrotoluene does not form a compound; the eutectic, m. p. 55°, corresponds with 34% of picric acid. Further, camphor does not combine with 2:4:6-trinitrotoluene, but forms a simple eutectic, m. p. about 52°.

Uncertainty still prevails as regards the exact melting point of picric acid, and it would appear advantageous to employ in its place the solidifying point, for which more concordant results are obtainable.

T. H. P.

Action of Aromatic Alcohols on Aromatic Compounds in the Presence of Aluminium Chloride. I. RALPH C. HUSTON and THEODORE E. FRIEDEMANN (*J. Amer. Chem. Soc.*, 1916, 38, 2527—2533).—When benzene is mixed with benzyl alcohol in equimolecular proportions and anhydrous aluminium chloride is added, a vigorous action occurs, the products being diphenylmethane, *p*-dibenzylbenzene, *o*-dibenzylbenzene, a hydrocarbon, C₂₇H₂₄, which is either tribenzylbenzene or methylenebisdiphenylmethane, CH₂Ph·C₆H₄·CH₂·C₆H₄·CH₂Ph, and anthracene. By increasing the proportion of benzene used with respect to the benzyl alcohol, the yield of diphenylmethane is increased and of anthracene reduced. A rather large proportion of aluminium chloride is necessary.

With the view of confirming Verley's hypothesis as to the mechanism of the reaction between chloromethyl ethyl ether and benzene in the presence of aluminium chloride (compare A., 1899, i, 207), the authors have examined the action of aluminium chloride on mixtures of benzyl ethyl ether and benzene, chloromethyl ethyl ether and benzene, and on chloromethyl ethyl ether alone. In the first case, the products of the reaction were the same as with benzyl alcohol and benzene, but even at the end of a week 15% of unchanged benzyl ethyl ether was recovered. In the second case no benzyl ethyl ether was obtained. In the last case formaldehyde was obtained. They suggest as an alternative to Verley's hypothesis that the reaction is due to the preliminary formation of formaldehyde from the chloromethyl ethyl ether, and that this then reacts with the benzene to give diphenylmethane and anthracene.

W. G.

Amines. VI. The Utilisation of Hypochlorite Colour Reactions in Establishing the Mechanism of the Action of Methyl Sulphate on Aniline. NORMAN A. SHEPARD (*J. Amer. Chem. Soc.*, 1916, 38, 2507—2514).—A careful examination of the action of methyl sulphate on aniline shows that the

course of the reaction is not that given by Werner (T., 1914, 105, 2762), but that Ullmann's theory (compare A., 1903, i, 394) is correct. Using equimolecular proportions of the base and the sulphate as directed by Werner, the crystalline additive product was found to be the methyl hydrogen sulphate of the unalkylated base, $C_6H_7NH_2 \cdot MeHSO_4$, the yield being in accord with Ullmann's theory. Using Werner's quantities, the reaction at first proceeds according to the equation $2NH_2Ph + 2Me_3SO_4 = NH_2Ph \cdot MeHSO_4 + NHMePh + Me_2SO_4$. The methylaniline is then converted into its methyl hydrogen sulphate,

$2NHMePh + Me_2SO_4 = NHMePh \cdot MeHSO_4 + NMe_2Ph$,
and finally the dimethylaniline gives a methyl hydrogen sulphate.

The author has carefully examined the colour reactions of aniline and its methyl and dimethyl derivatives under differing conditions, and finds that the colours obtained vary considerably with the conditions. The characteristic test for aniline is the deep reddish-purple colour obtained by the addition of bleaching powder solution to a neutral aqueous solution of the base, and under these conditions methylaniline gives a yellow, murky solution, and dimethylaniline a colourless, murky solution. If the addition of the hypochlorite is followed by the addition of dilute sulphuric acid, methylaniline gives a very intense indigo-blue colour, and dimethylaniline a deep orange-yellow colour, both these colours being characteristic. If the acid is added first the same colour reactions occur, but the shade is not so intense in the case of methylaniline. In alkaline solution, methylaniline gives with bleaching powder solution a white precipitate with distinct navy-blue colour, developing slowly and then slowly fading to yellow, which is characteristic. W. G.

The Molecular Rearrangement of Triphenylmethylhalogenamines. ISABELLA VOSBURGH (*J. Amer. Chem. Soc.*, 1916, 38, 2081—2095).—A number of triphenylmethylhalogenamines were prepared and their molecular rearrangements under various conditions studied with the view of obtaining fresh evidence in favour of Stieglitz's theory (compare this vol., i, 22) as to the method of these arrangements. *Triphenylmethylbromoamine*, $CPh_3 \cdot NHBr$, m. p. 63° , was prepared by brominating triphenylmethylamine in cold chloroform solution in the presence of 10% sodium hydroxide. It is reconverted by dry hydrogen chloride into triphenylmethylamine hydrochloride. When heated with soda-lime, calcium oxide, or sodium methoxide in methyl-alcoholic solution, the bromoamine is converted into phenyliminobenzophenone, $CPh_3 \cdot NPh$. Triphenylmethylamine was converted into its *benzoyl* derivative, m. p. 160 — 162° , in order to be able to test for the presence of this substance in the products of the previous rearrangement.

When triphenylmethylamine was added to a cold solution of hypochlorous acid and the mixture extracted with chloroform, *triphenylmethylchloroamine*, $CPh_3 \cdot NCl_2$, m. p. 128° , was obtained, but all attempts to prepare the monochloroamine were unsuccessful.

This substance underwent molecular rearrangement when heated alone or with soda-lime, and in the latter case phenyliminobenzophenone was isolated from the products of the reaction.

Triphenylmethylmethylchloroamine, $\text{CPh}_3\cdot\text{NMeCl}$, m. p. 102—104°, was prepared by the action of hypochlorous acid on triphenylmethylmethylamine hydrochloride in aqueous alcoholic solution. Attempts to cause it to undergo molecular rearrangement by the action of heat or alkalis were unsuccessful.

Diphenyl-p-chlorophenylmethylamine was prepared from the corresponding chloride, m. p. 86—89°, by passing dry ammonia gas into its hot benzene solution, and isolated in the form of its *hydrochloride*, m. p. 185—186°, giving a *platinichloride*, m. p. 155°. The hydrochloride was converted by the action of hypochlorous acid into *diphenyl-p-chlorophenylmethyldichloroamine*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CPh}_2\cdot\text{NCl}_2$, m. p. 110—112°, which by the action of heat alone or with soda-lime underwent molecular rearrangement, giving phenyliminobenzophenone and chlorophenyliminobenzophenone in the molecular proportion of 3:1.

Attempts to cause a molecular rearrangement of benzophenone-chloroimide, $\text{CPh}_2\cdot\text{N}\cdot\text{Cl}$, which should by its constitution readily suffer this, according to Beckmann's theory, either by passing chlorine over the heated substance or by the action of phosphorus pentachloride, were unsuccessful.

W. G.

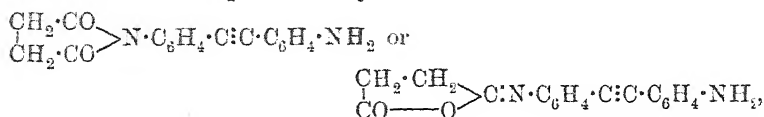
The Molecular Rearrangement of some Triarylmethylchloroamines. AGNES FAY MORGAN (*J. Amer. Chem. Soc.*, 1916, 38, 2095—2101).—An extension of Vosburgh's work (compare preceding abstract), a quantitative study being made of the molecular rearrangement of two substituted triphenylmethylchloroamines under the influence of soda-lime.

Phenyl-p-dichlorophenylmethylamine hydrochloride, m. p. 201°, was prepared by the action of dry ammonia gas on a hot benzene solution of phenyldi-*p*-chlorophenylmethyl chloride (compare Stagner, this vol., i, 23). By the action of hypochlorous acid this was converted into *phenyldi-p-chlorophenylmethylchloroamine*, $\text{CPh}(\text{C}_6\text{H}_4\text{Cl})_2\cdot\text{NHCl}$, m. p. 55°, which when heated with soda-lime gave a mixture of phenylimino-*pp'*-dichlorobenzophenone and *p*-chlorophenylimino-*p*-chlorobenzophenone in the molecular proportions of 1:2.

Phenyl-*p*-chlorophenyl-*p*-bromophenylmethyl chloride (compare Stagner, *loc. cit.*) was converted by the action of ammonia into *phenyl-p-chlorophenyl-p-bromophenylmethylamine*, isolated in the form of its *hydrochloride*, m. p. 196°, which by the action of hypochlorous acid was converted into *phenyl-p-chlorophenyl-p-bromophenylmethylchloroamine*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CPh}(\text{C}_6\text{H}_4\text{Br})\cdot\text{NHCl}$, not obtained in a solid form. This substance when heated with soda-lime gave a mixture of *p*-chlorophenylimino-*p*-bromobenzophenone, *p*-bromophenylimino-*p*-chlorobenzophenone, and phenylimino-*p*-chloro-*p'*-bromobenzophenone in equimolecular proportions.

W. G.

Rings containing a Triple Linking. III. Constitution of *cyclo*Succinyldiaminotolane. PAUL RUGGLI (*Annalen*, 1916, 412, 1—13. Compare A., 1912, i, 914; 1913, i, 1106).—The object of the present investigation is to show that *cyclosuccinyldiaminotolane* cannot be represented by the constitution



either of which is possible in view of the method of preparation of the substance.

o'-Nitro-*o*-aminotolane, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \equiv \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, ruby-red needles, m. p. 118—119°, obtained together with *oo*'-diaminotolane and unchanged material by heating *oo*'-dinitrotolane with phenylhydrazine in xylene at 125—150°, is a weak base which forms a colourless *hydrochloride*, can be diazotised, and yields *oo*'-diaminotolane by further reduction. When treated with succinyl chloride under the conditions in which *oo*'-diaminotolane yields *cyclosuccinyldiaminotolane*, it is converted, not into a substance having a constitution corresponding with either of those given above, but into *di-o*'-nitrosuccinyldi-*o*-aminotolane, $\text{C}_2\text{H}_4(\text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \equiv \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$, tufts of yellow needles, m. p. 227—229° (decomp.).

o'-Nitro-*o*-aminotolane reacts with the hemi-chloride of ethyl succinate in boiling ether to form the *ester*,

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \equiv \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, yellow needles, m. p. 122.5—123.5°; attempts to convert this into a substance having a constitution corresponding with the former of those given above were unsuccessful, since by heating in a vacuum the substance remains practically unchanged at 240° and yields a pitch at higher temperatures. The failure to effect ring closure is probably to be attributed to the presence of a substituent in the ortho-position to the nitrogen atom. The *o*-toluidide, $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, prepared from *o*-toluidine and the hemi-chloride of ethyl succinate in ether, also does not lose ethyl alcohol at 300°, whereas the *anilide*,

$\text{NHPh} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, m. p. 56.5—57.5°, prepared in a similar manner, is converted into succinanil by heating at 220° for a few minutes.

The fact that succinyl chloride and aniline in cold dilute solution do not react to form succinanil is regarded as disproving the possibility that *cyclosuccinyldiaminotolane* may have either of the two formulæ given above. C. S.

Molecular Rearrangements of β -Triphenylmethyl- β -methylhydroxylamines and the Theory of Molecular Rearrangement. JULIUS STIEGLITZ and BERT ALLEN STAGNER (*J. Amer. Chem. Soc.*, 1916, 38, 2046—2068).—An exhaustive investigation has been made of the reaction examined by Stieglitz and Leech (A., 1914, i, 268), and it is now definitely shown that

methylaniline is formed in quantity by the hydrolysis of the product of the rearrangement of β -triphenylmethyl- β -methylhydroxylamine, and further that benzophenone is also obtained during this hydrolysis.

β -Diphenyl- p -bromophenylmethyl- β -methylhydroxylamine was prepared in the form of its hydrochloride by condensing diphenyl- p -bromophenylmethyl chloride with methylhydroxylamine hydrochloride. The free base, prepared by the addition of alkali to the hydrochloride, was heated on a water-bath in ethereal solution with phosphorus pentachloride for four hours, and from the product of rearrangement, on hydrolysis, methylaniline and bromomethylaniline hydrochlorides, benzophenone, and bromobenzophenone were isolated.

In the light of this and other recent work (compare Kuhara, A., 1914, i, 538; Jones, A., 1914, i, 253), the authors discuss very fully the various theories as to the mode of rearrangement in such reactions. They draw the conclusion that unless conclusive evidence is brought that salts, leading to the intermediate formation of salts of univalent nitrogen derivatives, are involved in their rearrangement, the rearrangement of triphenylmethylmethylhydroxylamine, the relation of stereoisomerism of oximes to their arrangement products, and the spontaneous rearrangement of the sulphonic ester of benzophenoneoxime (compare Kuhara, *loc. cit.*) would be inconsistent with the theory of the intermediate formation of univalent nitrogen derivatives in the rearrangement of hydroxylamines, and that the facts at present agree with Beckmann's theory of a direct exchange of radicles. Other facts, such as the rearrangement of azides, are, however, inconsistent with Beckmann's theory, but are in agreement with Stieglitz's theory (*loc. cit.*) of the intermediate formation of unsaturated nitrogen derivatives in the rearrangements of chloroamines, hydroxylamines, and azides. It is probable that both types of arrangements may take place. Common to both theories, and the most important feature in their present forms, is that the rearrangements originate from the tendency of unstable positive atoms, Cl^+ , $-\text{O}^+$, $=\text{N}^+$, etc., to pass over into their stable negative forms, Cl^- , $-\text{O}^-$, N^- , by a capture of electrons from other atoms in the same molecule.

W. G.

The Molecular Rearrangement of Triarylmethylhydroxylamines. BERT ALLEN STAGNER (*J. Amer. Chem. Soc.*, 1916, 38, 2069—2081).—A continuation of the study of the molecular rearrangement of halogenated triphenylmethylhydroxylamines under the influence of phosphorus pentachloride (compare preceding abstract). A quantitative examination of the products of hydrolysis of the phenyliminobenzophenones resulting from the rearrangement was made to determine the proportions of each aryl group migrating and the influence of substitution on this migration. Of the three hydroxylamines examined, diphenyl- p -bromophenylmethylhydroxylamine, like the corresponding chloro-compound, rearranged itself so that, roughly, in two-thirds of the rearranging

molecules a phenyl group, and in the remaining third a bromophenyl group, migrated. This ratio was reversed in the case of phenyl-dibromo- and -dichlorophenylmethylhydroxylamine. In the case of phenylchlorophenylbromophenylmethylhydroxylamine, roughly one-third of the rearranging molecules showed a migration of the chlorophenyl group, the bromophenyl group, and the phenyl group respectively. These results indicate that the halogens have no marked effect on the tendency of the aryl groups to migrate to the nitrogen.

Diphenyl-p-bromophenylmethylhydroxylamine was obtained by the interaction of diphenyl-*p*-bromophenylmethyl chloride in anhydrous benzene and hydroxylamine in concentrated alcoholic solution, and isolated in the form of its *hydrochloride*, m. p. 144—145° (decomp.). The free base is a pale yellow, viscous liquid.

Phenyl-di-p-chlorophenylmethylhydroxylamine hydrochloride, m. p. 129—130° (decomp.), was similarly prepared. The free base is a pale yellow, syrupy liquid or gum.

Phenyl-di-p-bromophenylmethylhydroxylamine hydrochloride has m. p. 75°. The free base is a yellow, viscous liquid.

The fourth hydroxylamine was prepared by the following process. *p*-Chlorobenzophenone dichloride was condensed with bromobenzene in the presence of aluminium chloride, the mixture being then poured on to ice. From the products, *phenyl-p-chlorophenyl-p-bromophenylcarbinol*, m. p. 91—93°, was isolated and converted into its *chloride*, m. p. 69—72°, by passing hydrogen chloride into a solution of the carbinol in carbon disulphide. This chloride was condensed with hydroxylamine as in the previous two cases, giving *phenyl-p-chlorophenyl-p-bromophenylmethylhydroxylamine hydrochloride*, softening at 45°, no sharp m. p. The free base was a yellow syrup. W. G.

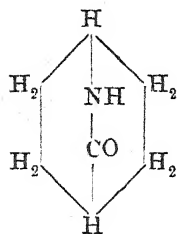
Aromatic Esters of Sulphurous Acid. M. M. RICHTER (*Ber.*, 1916, 49, 2339—2345).—Aromatic esters of sulphurous acid are readily obtained by the action of thionyl chloride on the phenols in the presence of pyridine and in carbon disulphide solution. Diphenyl and ditolyl sulphites are stable, but the introduction of negative substituents lowers the stability. A new class of compounds is obtained if the sulphites are treated with sulphuric acid, and this reaction will be discussed in a future communication.

Phenyl sulphite, $\text{SO}(\text{OPh})_2$, is a pale straw-yellow liquid, b. p. 185° (corr.)/15 mm. (slight decomposition; the crude substance is purer); *o*-tolyl sulphite has b. p. 192° (corr.)/13 mm., *m*-tolyl sulphite, b. p. 195—196° (corr.)/12 mm., and *p*-tolyl sulphite, b. p. 199° (corr.)/12 mm.; all are very stable towards water, alkali hydroxides, or ammonia. *Benzyl sulphite*, b. p. 193—199°/15 mm. (much decomposition), and *thymyl sulphite* are refractive oils. *α -Naphthyl sulphite*, m. p. 92—93°, is very stable towards alkalis, but is immediately hydrolysed by alcoholic ammonia, whilst *β -naphthyl sulphite*, a nearly powder, m. p. 79°, is very susceptible even to moisture. *p*-Chlorophenyl sulphite, b. p. 213—214°/12 mm., 2:4:6-trichloro-

phenyl sulphite, m. p. 87—88°, and 2:4:6-*tribromophenyl sulphite*, m. p. 130° (decomp.), are very susceptible to the influence of water and cannot be preserved. J. C. W.

The Silver Salt of Tri-iodophenol and its Catalytic Decompositions. G. H. WOOLLETT (*J. Amer. Chem. Soc.*, 1916, 38, 2474—2478).—The author has prepared the silver salt of tri-iodophenol in a very pure state, but all the samples were yellow, and attempts to prepare Hantzsch's colourless form (compare A., 1908, i, 17) were unsuccessful. The salt when warmed with ethyl iodide decomposes in a manner exactly similar to that of the silver salt of tribromophenol (compare Hunter, A., 1916, i, 717), giving silver iodide and an unsaturated residue which polymerises to a white, amorphous oxide, $(C_6H_2OI_2)_n$. When treated with a very little iodine in water, the silver salt gives the red substance described by Lautemann (*Annalen*, 1861, 120, 309). W. G.

Catalytic Hydrogenation of Hydroxy- and Amino-benzoic Acids. J. HOUBEN and ALEXANDER PFAU (*Ber.*, 1916, 49, 2294—2299).—It is unnecessary to use glacial acetic acid as a solvent in the catalytic reduction of hydroxy- and amino-benzoic acids; in fact, it is very advisable not to do so, for these compounds suffer loss of water or ammonia to a considerable extent under such conditions. Even though the acid and its reduction product may be almost insoluble in water, they may be very easily reduced in suspension by hydrogen in the presence of platinum-black. Thus, *p*-aminobenzoic acid may be quantitatively reduced to *p*-aminocyclohexanecarboxylic acid, which crystallises with 0.5H₂O and sublimates at above 330°, but if quickly heated changes into the *lactam* (isonortropinone) (annexed formula), a very bitter substance, which forms very long needles, m. p. 191—192°.



Salicylic and anthranilic acids have also been reduced by this means, and accounts of many other applications of the process and of the products are promised. J. C. W.

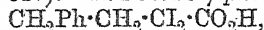
Salts and Esters of the Nitrophenylacetonitriles. ST. OPOLSKI, Z. KOWALSKI, and J. PILEWSKI (*Ber.*, 1916, 49, 2276—2283).—During recent years, the authors have isolated dark-coloured *potassium*, *sodium*, *silver*, and *methyl* salts of the three nitrophenylacetonitriles, similar to those obtained by Lifschitz and Jenner (A., 1916, i, 45). They regard them as being quinonoid in structure, especially in view of the fact that *o*- and *p*-nitrophenylacetic esters give similar salts (A., 1916, i, 815). The solutions are all violet, but become dark red or green in time.

o-Nitrophenylacetonitrile, m. p. 83.5—84°, is best obtained by Pschorr and Hoppe's method (A., 1910, i, 737), the necessary acetic acid being prepared by oxidising *o*-nitrophenylpyruvic acid, for which *o*-nitrotoluene is the starting point (Reissert, A., 1897,

i, 417). Attempts to prepare it from *o*-nitrobenzyl chloride or bromide, m. p. 42° , were fruitless. The para-compound, m. p. $115-116.5^{\circ}$, is obtained by nitration, and the meta-isomeride, m. p. $61-62^{\circ}$, from *m*-nitrobenzyl chloride.

In contrast with the violet methyl ester obtained from the freshly made silver salt (the *m*-ester is the most stable one), a colourless methyl compound can be formed by the action of methyl iodide on phenylacetoneitrile in the presence of powdered sodium hydroxide, followed by nitration. This is α -*p*-nitrophenylpropionitrile, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{CN}$, m. p. $73-75^{\circ}$. J. C. W.

Semicarbazones of α -Ketonic Acids. α , α -Di-iodo- and Di-bromophenylbutyric Acids; α -Iodo- and α -Bromophenylcrotonic Acids. J. BOUGAULT (*Compt. rend.*, 1916, **163**, 481—483. Compare A., 1916, i, 817).— α , α -Di-iodo- γ -phenylbutyric acid,



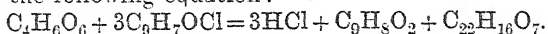
m. p. 145° , is readily obtained by the action of iodine on an alkaline solution of the semicarbazone of benzylpyruvic acid, and is isolated in the form of its sodium salt. An aqueous solution of its sodium salt, when heated at 100° , rapidly decomposes, giving the two α -iodo- γ -phenylcrotonic acids, $\text{CH}_3\text{Ph}\cdot\text{CH}\cdot\text{Cl}\cdot\text{CO}_2\text{H}$, of which the stable form has m. p. 105° and the labile form m. p. 100° . The labile acid is converted into the stable form by heating it at 100° for two hours with dilute hydrochloric acid.

α , α -Dibromo- γ -phenylbutyric acid, m. p. 134° , is obtained as its sodium salt by the action of sodium hypobromite on a solution of the semicarbazone of benzylpyruvic acid. Like the di-iodo-compound, it is readily decomposed, giving two α -bromo- γ -phenylcrotonic acids, the stable form of which has m. p. 96° and the labile form m. p. 100° . The labile form is readily converted into the stable acid by the addition of a trace of bromine to its solution in carbon disulphide.

Both the α -iodo- and the α -bromo-phenylcrotonic acids readily yield γ -phenylcrotonic acid. W. G.

The Cinnamates of Tartaric Acid. The Question of Optically Active Cinnamic Acids. EMIL ERLENMEYER and G. HILGENDORFF (*Biochem. Zeitsch.*, 1916, **77**, 55—89).—It has been shown that when cinnamic acid is heated with tartaric acid at 168° an amorphous product soluble in sodium carbonate is obtained, which contains cinnamates. When cinnamoyl chloride or cinnamic anhydride is employed, products of similar physical properties are also obtained. If, however, *d*-tartaric acid is heated only at $105-110^{\circ}$ with cinnamoyl chloride, the fused mass, after a certain interval, solidifies; a product is thereby obtained, which, instead of being levorotatory, is dextrorotatory, and is, furthermore, insoluble in sodium carbonate. It can be recrystallised from light petroleum, and yields a product, m. p. $158-159^{\circ}$, with $[\alpha]_D + 282.5^{\circ}$ in acetone solution. This is the anhydride of the dicinnamate of tartaric acid, $\text{C}_{22}\text{H}_{16}\text{O}_7$. On heating alone above 110° , it is not converted into a levorotatory product. If, however, the solidified

product from the original fusion, made at 105—110° is heated at 168°, an amorphous, levorotatory product is obtained. Further investigation has shown that the dextrorotatory anhydride readily undergoes conversion when kept in solvents (chloroform or acetone) containing water into a levorotatory, crystalline substance soluble in sodium carbonate, which can be recrystallised from benzene. This has m. p. 166—167°, and $[\alpha]_D -275^\circ$ in solution in sodium carbonate, and is the dicinnamate of tartaric acid, $C_{22}H_{18}O_8$. When the above reaction is carried out by heating together one molecule of tartaric acid with two molecules of cinnamoyl chloride, it is found that about one-third of the tartaric acid is recovered unchanged. A better yield is obtained when one molecule of tartaric acid is heated with three molecules of the chloride, and in this case cinnamic acid is obtained as a product of the reaction. This must therefore be represented by the following equation:



When cinnamoyl chloride is heated under similar conditions with *l*-tartaric acid, an anhydride of a dicinnamate is also obtained. This is similar in its properties to the anhydride described above, but it is levorotatory instead of dextrorotatory, the levorotation and dextrorotation of the two substances being very nearly equal. The *l*-anhydride is also readily converted into a dicinnamate of tartaric acid, which is dextrorotatory, the dextrorotation being nearly equal to the levorotation of the corresponding substance from *d*-tartaric acid.

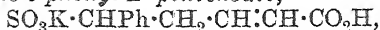
The mechanism of the reaction between cinnamoyl chloride and the tartaric acids is discussed in some detail by the authors.

S. B. S.

Preparation of Carboxydisulphonic Acids from the Bisulphite Compounds of Unsaturated Aldehydes and Malonic Acid. OTTO NOTTBOHM (*Annalen*, 1916, 412, 49—78).—In the reaction between malonic acid and the sodium hydrogen sulphite compound of glyoxal described by Behrend and ten Doornkaat Koolman (*A.*, 1913, i, 8) the malonic acid cannot be replaced by methylmalonic, succinic, phenyl- or nitrophenyl-acetic acid, and the aldehyde must be such that its bisulphite compound is not, or at least not easily, hydrolysed under the experimental conditions. Such aldehydes are unsaturated ones which combine with two molecules of alkali hydrogen sulphite, and the behaviour of these additive compounds with malonic acid and with potassium hydrogen malonate has been examined.

When potassium α -hydroxy- γ -phenylpropane- $\alpha\gamma$ -disulphonate, prepared by heating at 130° the residue obtained by evaporating the solution of cinnamaldehyde (1 mol.) in boiling concentrated potassium hydrogen sulphite (2 mols.), is boiled with an equal molecular quantity of malonic acid and water for some time, sulphur dioxide is evolved and a by-product crystallises, even while the solution is boiling, the two main products, however, remaining in the cold mother liquor. The by-product proves to be *potassium*

hydrogen δ -sulpho- δ -phenyl- Δ^{α} -pentenoate,



anhydrous needles; the *calcium* and the *barium* salts are described, and from the latter the free acid is obtained as a viscous syrup. When the acid or the potassium salt in aqueous solution is treated with bromine, addition, followed by elimination of hydrogen bromide, appears to occur, and α -bromo- δ -sulpho- δ -phenyl- Δ^{α} -pentenoic acid, $\text{SO}_3\text{H} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CH} : \text{CBr} \cdot \text{CO}_2\text{H}$, colourless needles, decomp. $203-205^\circ$, is obtained, which dissolves only slowly in aqueous sodium carbonate and forms a *methyl* ester, m. p. $165-166^\circ$, and *ethyl* ester, $\text{C}_{13}\text{H}_{15}\text{O}_5\text{BrS}$, m. p. $162-163.5^\circ$, both glistening leaflets insoluble in aqueous sodium carbonate.

The main products of the preceding reaction (which are the only products when potassium hydrogen malonate is used instead of malonic acid) remain in the mother liquor. By evaporating the solution to dryness, heating the residue at 150° for some hours (whereby carbon dioxide is evolved), and crystallising the product from glacial acetic acid, two substances are obtained. The one which is the less soluble is *dipotassium hydrogen $\beta\delta$ -disulpho- δ -phenylvalerate*, $\text{SO}_3\text{K} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CH}(\text{SO}_3\text{K}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, needles, whilst the more soluble is an isomeric salt which could not be obtained crystalline. The respective acids, obtained by means of concentrated hydrochloric acid, are viscous syrups, from which the only crystalline derivatives obtainable are the *aniline* salts of the *anilidodisulphonic acids*,

$\text{NH}_2\text{Ph} \cdot \text{SO}_3\text{H} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CH}(\text{SO}_3\text{H} \cdot \text{NH}_2\text{Ph}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$, m. p. $240-242^\circ$ (decomp.), quadratic leaflets, and $278-281^\circ$ (decomp.), slender needles, respectively, prepared by boiling the acids with aniline. By fusion with potassium hydroxide and a little water on the water-bath the anilides both yield the same substance, $\text{C}_9\text{H}_8\text{O}$, colourless needles, m. p. 188° , the constitution of which has not yet been determined. If hydrolysed with boiling 20% hydrochloric acid before being fused with potassium hydroxide the two anilides, as do also the two acids under the same conditions, yield cinnamylacrylic (δ -phenyl- $\Delta^{\alpha\gamma}$ -pentadienoic) acid. The two sulpho-groups in the two acids are assumed to be in the β - and δ -positions, and the two acids are assumed to be stereo-isomeric.

By treatment similar to that described above, potassium α -hydroxypropyl- $\alpha\gamma$ -disulphonate (from acraldehyde and potassium hydrogen sulphite) and potassium hydrogen malonate or malonic acid also yield two salts, one of which is *dipotassium hydrogen $\beta\delta$ -disulphovalerate*, $\text{SO}_3\text{K} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{SO}_3\text{K}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, crystals, whilst the other isomeric salt has only been obtained as a syrup. The acids prepared from these two salts are syrups, and only that prepared from the crystalline salt yields the *aniline* salt of the *anilido-acid*,

$\text{NH}_2\text{Ph} \cdot \text{SO}_3\text{H} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{SO}_3\text{H} \cdot \text{NH}_2\text{Ph}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$, crystals, m. p. $239-242^\circ$ (decomp.). Both acids yield vinylacrylic ($\Delta^{\alpha\gamma}$ -pentadienoic) acid by fusion with potassium hydroxide on the water-bath.

The reaction between dipotassium α -hydroxybutane- $\alpha\gamma$ -disulphonate (from crotonaldehyde and potassium hydrogen sulphite) and malonic acid or potassium hydrogen malonate appears to yield only one acid, $\beta\delta$ -disulphohexzoic acid,

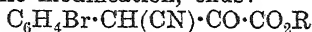


a brown syrup, of which the only crystalline derivative obtained is the *aniline* salt of the *anilido-acid*,

$\text{NH}_2\text{Ph}\cdot\text{SO}_3\text{H}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{SO}_3\text{H}, \text{NH}_2\text{Ph})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$,
rectangular leaflets, m. p. 245—248° (decomp.). The latter yields a substance, $\text{C}_6\text{H}_6\text{O}$, quadratic leaflets, m. p. 155—156°, by fusion with potassium hydroxide and a little water on the water-bath, but when hydrolysed with hydrochloric acid previously to the fusion yields sorbic acid in about 50% yield; the crude potassium disulphohexzoate also yields sorbic acid to about the same extent by fusion with potassium hydroxide as above. C. S.

Desmotropic Forms of Bromocyanophenylpyruvic Esters.

ST. OPOLSKI, L. CZAPOROWSKI, and J. ZACHARSKI (*Ber.*, 1916, **49**, 2283—2292).—The influence of a carbonyl group in the side-chain on the ability of phenylacetonitrile to exist in tautomeric forms has been examined. Both ethyl *o*-bromocyanophenylpyruvate and the *p*-bromo-compound can be isolated in a colourless ketonic form and a coloured enolic modification, thus:



and $\text{C}_6\text{H}_4\text{Br}\cdot\text{C}(\text{CN})\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{R}$.

Ethyl oxalate and *p*-bromophenylacetonitrile are warmed with a solution of sodium ethoxide, and the sodium salt of the *ethyl p*-bromocyanophenylpyruvate separates on cooling. The *keto*-ester is obtained in colourless crystals, m. p. 147·5°, if a solution of this salt is acidified with acetic acid, but the *enolic* ester is deposited if a solution in an excess of alkali hydroxide is mixed with dilute hydrochloric acid at 0°, as an orange-coloured precipitate, m. p. 60° (decomp.). The enol dissolves quickly in sodium carbonate solution, and reacts with bromine and ferric chloride, but the ketone dissolves slowly and does not give the other reactions. The *sodium*, *potassium*, *ammonium*, and *silver* salts are yellow; phenylhydrazine gives bromine-free compounds, m. p. 260° and m. p. 119—120°, under some conditions, but the true *phenylhydrazone* is formed in yellow crystals, m. p. 118°, if a concentrated solution of the ester in acetic acid is warmed with one equivalent of the base.

o-Bromophenylacetonitrile, m. p. 0—1°, b. p. 145—147°/14 mm., reacts in the same manner to form *ethyl o*-bromocyanophenylpyruvate; the colourless *keto*-ester has m. p. 140—142°, the yellow *enolic* ester has m. p. 98—120° (decomp.), whilst the *sodium* and *silver* salts are pale yellow. The phenylhydrazone could not be isolated, the products being the above compounds, m. p. 260° and m. p. 119—120°, which are recognised as the diphenylhydrazide of oxalic acid and the phenylhydrazide of ethyl hydrogen oxalate.

In the preparation of the enolic ester the precipitate is quickly removed by filtration. It is then observed that colourless crystals,

m. p. 82° , are deposited by the mother liquor, which change after contact with the solution for a longer time into others with m. p. $148-150^{\circ}$. These two substances are free from nitrogen, and are probably desmotropic forms of *o*-bromophenyloxalacetic acid, $C_6H_4Br \cdot CH(CO_2H) \cdot CO \cdot CO_2H$. J. C. W.

Diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic Acid and Trichlorodiethylaminoxanthonecarboxylic Acid and some of their Derivatives. W. R. ORNDORFF and C. C. ROSE (*J. Amer. Chem. Soc.*, 1916, **38**, 2101—2119. Compare Basler Chemische Fabrik., 1896, D.R.-P., 85931, 87068; Haller and Umbgrove, A., 1901, i, 644).—An investigation as to the best method of preparing diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid and of its properties.

When diethyl-*m*-aminophenol is condensed with tetrachlorophthalic anhydride under such conditions that tetrachlororhodamine is not formed, either by heating the two substances in toluene according to the German method (*loc. cit.*) or by heating them together without a solvent (compare Haller and Umbgrove, *loc. cit.*), the product is made up of two molecules of the aminophenol and one of the anhydride, and not of one molecule of each substance as stated by the latter authors. The product is *hydroxyphenyldiethylammonium diethylamino-m-hydroxybenzoyltetrachlorobenzoate*,

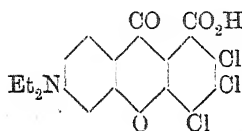
$OH \cdot C_6H_3(NEt_2) \cdot CO \cdot C_6Cl_4 \cdot CO_2 \cdot NHEt_2 \cdot C_6H_4 \cdot OH$, prisms having a faint yellow tinge, m. p. 198° (decomp.). It dissolves in alkali or ammonium hydroxides with a yellow colour, which gradually darkens, and after a time the trichloro-acid (see below) is deposited as a bright yellow precipitate. The benzoate, if dissolved in cold 5% aqueous sodium hydroxide and the solution immediately poured into dilute sulphuric acid, or dissolved in cold concentrated sulphuric acid and the solution poured into ice water, is decomposed, giving diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid, light yellow prisms, m. p. 217° , already described by the previous workers (*loc. cit.*). When dry ammonia is passed over this acid it absorbs two molecules of the ammonia, losing one again when dry air is passed over it, giving an *ammonium* salt. It forms a yellow *silver* salt, a pale yellow *methyl* ester, m. p. $146-148^{\circ}$, and an *ethyl* ester, m. p. 120° . When heated with acetic anhydride on a water-bath for seven hours the acid gives a mixture of a true *diacetate*, $CO \begin{array}{c} \diagup O \\ \diagdown \end{array} \begin{array}{c} C_6Cl_4 \\ \diagup OAc \end{array} C \begin{array}{c} \diagup OAc \\ \diagdown \end{array} C_6H_3(NEt_2) \cdot OAc$, m. p. $230-231^{\circ}$, which is colourless, and a *monoacetate*,

$OAc \cdot C_6H_3(NEt_2) \cdot CO \cdot C_6Cl_4 \cdot CO \cdot OAc$, of the mixed anhydride of the tetrachloro-acid and acetic acid, which is yellow and has m. p. $174-180^{\circ}$, the true diacetate being a derivative of the tautomeric form of the acid; the absence of colour is due to the fact that the ketonic group is no longer present. The monoacetate when boiled for six hours with ethyl alcohol gave the *ethyl* ester of the true monoacetate, m. p. $190-192^{\circ}$, and with

methyl alcohol the *methyl* ester, m. p. 152—155°, both of which were yellow.

Dry hydrogen chloride, when passed over the dry tetrachloro-acid, is absorbed to the extent of slightly more than one molecule, giving a colourless substance, which when exposed to dry air loses its excess of acid and leaves a yellow *hydrochloride*. The excess of hydrogen chloride is loosely attached to the ketonic group, giving an oxonium or a carbonium salt. The methyl ester of the tetrachloro-acid takes up two molecules of hydrogen chloride under similar conditions, giving a colourless *dihydrochloride*, which when exposed to dry air loses one molecule of hydrogen chloride and gives a yellow *hydrochloride*. The methyl ester of the monoacetate of the tetrachloro-acid similarly gives a colourless *dihydrochloride*, which changes to a yellow *hydrochloride* with loss of hydrogen chloride.

When the tetrachloro-acid is dissolved in 3% aqueous potassium hydroxide and the solution is brought to the boil, the *potassium* salt of 2:3:4-trichloro-6-diethylaminoxanthone-1-carboxylic acid (annexed formula) is precipitated. It crystallises from methyl or ethyl alcohol in yellow needles, m. p. 285°, containing 2H₂O. The free acid is obtained by decomposing the potassium salt with hydrochloric acid in boiling aqueous solution. From methyl alcohol it is obtained with 1MeOH, yellow needles, m. p. 278°, and from ethyl alcohol with no solvent of crystallisation. From a suspension of the potassium salt in cold water the acid is precipitated as a *hydrate*,



$C_{17}H_{13}O_3NCl_3 \cdot CO_2H, H_2O$.

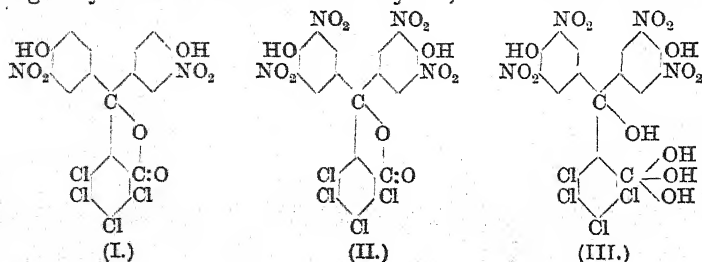
With dry ammonia the acid gives an *ammonium* salt, which is hygroscopic. When boiled with acetic anhydride, the free acid gives a mixed *anhydride*, $C_{17}H_{13}O_2NCl_3 \cdot CO \cdot OAc$, yellow needles, m. p. 188—190°, which is converted by boiling acetone into an *acetate*, a yellow powder, m. p. 185°. The mixed anhydride, when dried at 120°, gives a *hydrochloride*, which is pale yellow. When boiled with ethyl alcohol, the anhydride is converted into the free acid. Attempts to prepare a methyl ester of the trichloro-acid by the catalytic method of esterification were not successful. The dry trichloro-acid does not absorb hydrogen chloride, but concentrated hydrochloric acid turns it white without dissolving it.

W. G.

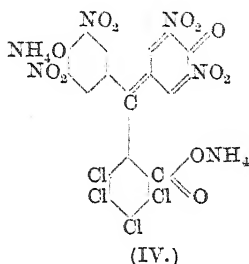
The Nitration Products of Phenoltetrachlorophthalein and some of their Derivatives. W. R. ORNDORFF and J. J. KENNEDY (*J. Amer. Chem. Soc.*, 1916, **38**, 2486—2503).—The authors have investigated the nitration products of phenoltetrachlorophthalein and their derivatives to study the effect of introducing negative groups into the phthalein molecule. The same yield of phenoltetrachlorophthalein (compare Orndorff and Black, A., 1909, i, 389) was obtained by using tetrachlorophthalic acid in place of the anhydride, and the same amount of tetrachlorofluoran

was also formed. When boiled with benzoyl chloride, phenoltetrachlorophthalein gives a *dibenzoate*, m. p. 213° , which crystallises from benzene as a *hydrate* containing $1\text{H}_2\text{O}$. This same *dibenzoate*, but no *monobenzoate*, is obtained by the Schotten-Baumann reaction. When phenoltetrachlorophthalein is heated with a mixture of glacial acetic acid (10 parts) and sulphuric acid (1 part) for one hour at 80° , the mixture cooled to 20° , and nitric acid (D 1.42) gradually added, keeping the temperature below 50° , *dinitrophenoltetrachlorophthalein*, light yellow crystals, m. p. 240° , is obtained, which is soluble in alkali hydroxides and carbonates, but insoluble in alkali hydrogen carbonates. The dinitro-compound when exposed to dry ammonia absorbs four molecules of ammonia, which it readily loses when exposed to air. It gives a *dibenzoate*, m. p. 205° , forming a *hydrate* containing $1\text{H}_2\text{O}$, and a *diacetate*, m. p. 136° , crystallising from benzene with $2\text{H}_2\text{O}$ and from acetone with $1\text{H}_2\text{O}$. When brominated in acetic acid solution, the liquid being heated until the dinitro-compound just dissolves, *bromodinitrophenoltetrachlorophthalein*, m. p. $220-221^{\circ}$, is obtained. It absorbs five molecules of ammonia, losing three when a current of dry air is passed over it. The diammonium salt is not stable and gradually loses ammonia when kept. *Dibromodinitrophenoltetrachlorophthalein* was obtained by using slightly more bromine and boiling the solution for two hours after all the dinitro-compound had dissolved. It has m. p. $271-272^{\circ}$ and is less soluble in the usual solvents than the monobromo-derivative. It absorbs five molecules of ammonia, losing three readily and the last two slowly when kept. When dinitrophenoltetrachlorophthalein is reduced in alcoholic solution by stannous chloride and hydrochloric acid, it yields *diaminophenoltetrachlorophthalein* as a coffee-brown, crystalline powder, m. p. above 335° , which dissolves in alkalis, giving a Prussian-blue colour, which disappears on keeping. The base gives a colourless *dihydrochloride*, which is dissociated by boiling its aqueous solution.

When phenoltetrachlorophthalein is heated for one hour at $80-90^{\circ}$ with sulphuric acid (D 1.84), the solution cooled to 0° , and a mixture of equal weights of nitric acid (D 1.42) and sulphuric acid added, the temperature being allowed to rise to 35° , the product is *tetranitrophenoltetrachlorophthalein*, pale yellow needles, m. p. $289-290^{\circ}$. It crystallises from acetone with $2\text{H}_2\text{O}$. In contact with dry ammonia it absorbs five molecules of the gas, losing only three in contact with dry air, the stable diammonium



salt being deep orange in colour. It gives a *dibenzoate*, m. p. 285°, and a *diacetate*, m. p. 200°, and on reduction yields *tetraaminophenoltetrachlorophthalein*, a light brown, crystalline powder, m. p. above 335°. It is more soluble in ordinary solvents than the diamino-compound, but its solutions in alkalis are not such an intense blue. Tetranitrophenoltetrachlorophthalein, unlike the dinitro-compound, is soluble in alkali hydrogen carbonates, as well as in the alkali hydroxides and carbonates. The authors assign the following constitutions to the dinitro- (formula I) and tetra-



nitro-derivatives (formula II), and consider that the dihydrate of the tetranitro-compound can be best represented as a hydrate of the carbinol carboxylic acid (formula III). The stable diammonium salt of the tetranitro-compound is best represented by the quinonoid formula (IV).

Of the nitro-compounds prepared, the tetranitro-compound has the strongest acid properties, the dinitro-compound the weakest, and the bromo-

dinitro- and dibromodinitro-compounds are intermediate between these two.

W. G.

Phthalonic Acid and its Derivatives. JOSEPH TCHERNIAC (T., 1916, 109, 1236—1243).—A description of certain reactions of phthalonic acid (Tcherniac, D.R.-P., 79693, 86914; Graebe and Trümpy, A., 1898, i, 318). Phthalonic acid behaves as a monobasic acid towards methyl-orange and as a dibasic acid towards phenolphthalein; it is readily oxidisable to phthalic acid, and when heated with acetic anhydride yields phthalonic anhydride, which reacts with a cold aqueous solution of ammonia, forming a *substance*, $C_8H_7O_4N$. A mixture of phthalonic acid, potassium hydroxide, and potassium cyanide in aqueous solution, when gradually saturated with carbon dioxide, gives the colourless *amide*,

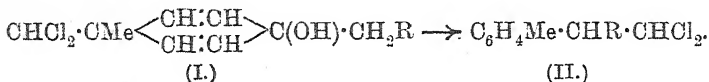
$CO \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot CO \cdot NH_2$, of phthalidecarboxylic acid. With sodium hydrogen sulphite in aqueous solution at 80°, sodium phthalonate yields a *sodium salt*, $C_8H_7O_5SNa \cdot H_2O$, which is converted by aqueous ammonia into a *substance*, $C_8H_7O_5N$, probably identical with aminophthalide. The constitution of the sodium salt is probably $C_6H_4 \langle \text{CH}(\text{SO}_3\text{Na}) \rangle \text{CO}$, $0.2H_2O$; in its formation a small quantity of a yellow *substance*, m. p. 232°, was obtained.

Details are given of a convenient bath to work at any constant temperature up to 400°, the contents of the bath consisting of potassium thiocyanate and water.

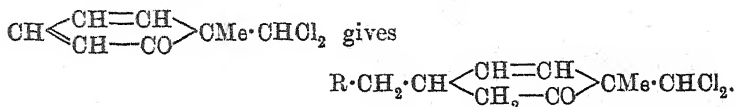
For experimental details the original should be consulted.

D. F. T.

The Hydroaromatic Ketones obtained from Phenols and Chloroform, and their Transformations. K. von AUWERS (*Ber.*, 1916, 49, 2389—2410. Compare A., 1907, i, 399; 1908, i, 550, etc.). It has already been shown that when 1-methyl-1-dichloromethyl- Δ^2 :5-cyclohexadien-4-one is treated with magnesium methyl or ethyl haloids, it is converted into carbinols of the formula I, which change on heating into benzenoid compounds of the formula II.



The reaction with other Grignard agents has now been investigated in order to see whether carbinols are always formed or whether, as in the case of the *o*-ketones, the radicle is introduced into the meta-position, thus:



It is found that the propyl, isopropyl, and benzyl compounds give carbinols in the normal way, but that in the case of the isopropyl derivative a small amount of an unsaturated ketone is also formed, according to the alternative scheme. Even the carbinol obtained in this case has peculiar properties, for the dichloroalkylbenzene which it yields on heating is a mixture of the expected one with another, in which the dichloromethyl group seems to be united directly to the ring.

1-Methyl-1-dichloromethyl- Δ^2 :5-cyclohexadien-4-one, from *p*-cresol, forms an *oxime*, in leaflets, m. p. 65°—66°. When treated with double the theoretical quantity of magnesium propyl bromide or iodide, it is transformed into 1-methyl-1-dichloromethyl-4-*n*-propyl- Δ^2 :5-cyclohexadien-4-ol, $\text{CHCl}_2 \cdot \text{CMe} \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} \text{CPr} \cdot \text{OH}$, which crystallises in white prisms, m. p. 79°, and changes on heating at 145° into *aa*-dichloro- β -*p*-tolylbutane, b. p. 134°/15 mm., D_4^{25} 1.1117, n_D 1.52404, n_D 1.52827, n_D 1.53900, n_D 1.54787 (all at 19.8°), and on boiling with alcoholic potassium hydroxide into β -chloro-4-methyl- α -ethylstyrene, $\text{C}_6\text{H}_4\text{Me} \cdot \text{C}(\text{Et})\text{CHCl}$, b. p. 117—118°/15 mm., D_4^{25} 1.0362, n_D 1.53639, n_D 1.54177, n_D 1.55548, n_D 1.56777 (at 19.85°). The styrene yields *p*-tolyl ethyl ketone on oxidation; b. p. 113°/14 mm., D_4^{25} 1.09883, n_D 1.52170, n_D 1.52692, n_D 1.54041, n_D 1.55267 (at 21.7°).

4-Benzyl-1-methyl-1-dichloromethyl- Δ^2 :5-cyclohexadien-4-ol, prepared in the same way from magnesium benzyl chloride, forms white needles, m. p. 94°, and yields *aa*-dichloro- β -phenyl- β -*p*-tolylethane, flat prisms, m. p. 94—95°, α -phenyl- α -*p*-tolylethane, b. p. 154—155.8°/14 mm., on reduction with sodium and alcohol, and β -chloro- α -phenyl-4-methylstyrene, m. p. 79—80°.

The crude product obtained by the action of magnesium isopropyl

bromide decomposes on being heated gradually to 160° , and then, on distillation, a large fraction, b. p. $141\text{--}143^{\circ}/13$ mm., and a smaller one, *, b. p. $160\text{--}180^{\circ}/13$ mm., may be obtained. The former is a mixture of dichlorides, one of which yields *p*-tert-butyltoluene on reduction with sodium and moist ether (b. p. 190° , D_{4}^{25} 0.8667, n_D 1.49118, n_D 1.49465, n_B 1.50513, n_Y 1.51400, at 13.25°), whilst the other gives an *aldehyde*, probably 2- or 3-methyl-4-isopropylbenzaldehyde, when the crude mixture is dissolved in cold concentrated sulphuric acid. The aldehyde is a fragrant oil, b. p. $122\text{--}123^{\circ}/14$ mm., $D_{4}^{17.4}$ 0.9813, n_D 1.53093, n_D 1.53628, n_B 1.55187, n_Y 1.56607, at 17.4° , undergoes oxidation to an *acid*, m. p. $91\text{--}92^{\circ}$, on exposure to the air, and forms a *semicarbazone*, in pearly leaflets, m. p. $206\text{--}209^{\circ}$.

It was anticipated that the dichloride would yield α -*p*-tolyl- α -methylpropaldehyde. This has been synthesised for comparison. *p*-Tolualdehyde is converted into *p*-methylmandelic acid, the *methyl* ester, m. p. $48\text{--}50^{\circ}$, is treated with magnesium methyl iodide, and so transformed into α -*p*-tolyl- β -methylpropan- α -diol, b. p. $168^{\circ}/14$ mm., m. p. $56.5\text{--}57.5^{\circ}$, and this is distilled with dilute sulphuric acid. α -*p*-Tolyl- α -methylpropaldehyde passes over as a pleasant smelling oil, b. p. $128\text{--}129^{\circ}/24$ mm., $D_{4}^{17.4}$ 0.9706, n_D 1.50815, n_D 1.51204, n_B 1.52340, n_Y 1.53297, at 17.4° , which forms a *semicarbazone*, m. p. 172° , and an *oxime* m. p. $73\text{--}74^{\circ}$.

The above fraction * consists of 1-methyl-1-dichloromethyl-2-isopropyl- Δ^5 -cyclohexen-4-one. It crystallises in stout prisms, m. p. 84° , forms a *semicarbazone*, m. p. $191\text{--}196^{\circ}$, a *p*-nitrophenylhydrazone, m. p. 185° , two isomeric *oximes*, stout prisms, m. p. $120\text{--}121^{\circ}$, and flat needles, m. p. $139\text{--}141^{\circ}$, a *dibromide*, m. p. $139\text{--}141^{\circ}$, and a *benzylidene* compound, silky needles, m. p. 173° .

J. C. W.

[**Action of Alcoholic Potassium Hydroxide on Ketones. III. Action of Alcoholic Potassium Hydroxide on Halogeno-amino-benzophenones and benzhydrols.** P. J. MONTAGNE (*Ber.*, 1916, 49, 2243—2262. Compare A., 1908, i, 988; 1913, i, 55).—The author continues his study of the influence of substituents on the reduction of benzophenones to benzhydrols by alcoholic potassium hydroxide and on the replaceability of halogen atoms in benzophenones. In the case of the bromobenzophenones, two reactions proceed simultaneously, but the speed of the one may be overwhelmingly greater than that of the other, according to the position of the halogen atom. Either bromine is eliminated and then the benzophenone is reduced to benzhydrol or the bromobenzophenone is reduced to bromobenzhydrol and nothing further takes place. Amino-groups have been shown to be a great hindrance to the reduction, and compounds containing both these and halogens have now been examined in order to find whether halogen atoms can counteract the effect of the amino-groups or amino-groups can prevent the elimination of halogen. Two halogen atoms in the *para*-positions will neutralise the influence of two amino-groups in the *meta*-positions.

The author believes that the time is now ripe for an exact quantitative re-examination of the whole problem.

p-Nitrobenzyl chloride condenses with chlorobenzene to form 2(?)-chloro-4'-nitrodiphenylmethane, m. p. 65°, b. p. 234°/17 mm., and 4-chloro-4'-nitrodiphenylmethane, m. p. 104·5°, b. p. 247°/19 mm. (compare Boeseken, A., 1904, i, 384), and the latter yields 4-chloro-4'-nitrobenzophenone on oxidation with chromic acid. This crystallises in pale yellow, triclinic-pinacoidal needles [$a:b:c=1:166:1:0:995$; $\alpha=125^{\circ}58'$, $\beta=128^{\circ}28'$, $\gamma=68^{\circ}22'$], m. p. 100·75°, b. p. 246°/12 mm., and may also be obtained from *p*-nitrobenzoyl chloride and chlorobenzene. The latter synthesis also gives rise to a small amount of 2(?)-chloro-4'-nitrobenzophenone, which may likewise be prepared by oxidising the corresponding diphenylmethane derivative; it separates in large, lustrous, wine-yellow, rhombic-bipyramidal crystals [$a:b:c=2:6857:1:1:7153$], m. p. 107·5°, b. p. 229°/10 mm., and may be reduced by means of stannous chloride to 2(?)-chloro-4'-aminobenzophenone, in stout, pale yellow, monoclinic-prismatic crystals [$a:b:c=0:5141:1:0:4824$; $\beta=81^{\circ}5'$], m. p. 112°. Similarly, 4-chloro-4'-aminobenzophenone is readily obtained in pale crystals, m. p. 104·5°, b. p. 262°/14 mm. This does not suffer reduction on boiling with alcoholic potassium hydroxide, and only a trace of halogen is eliminated.

The bromo-compounds may be obtained in the same way. 2(?)-Bromo-4'-nitrobenzophenone has m. p. 109·5°, b. p. 239°/10 mm., 4-bromo-4'-nitrobenzophenone has m. p. 125°, b. p. 264°/16 mm., 4-bromo-4'-aminobenzophenone has m. p. 196·5°, b. p. 279°/15 mm., and when boiled with alcoholic potassium hydroxide only suffers the loss of a trace of bromine.

3:3'-Diaminobenzophenone, m. p. 150—160°, b. p. 285°/11 mm., is partly reduced to the benzhydrol after boiling with alcoholic potassium hydroxide for two days. 4-Bromo-3:3'-diaminobenzophenone (following abstract) suffers loss of a considerable amount of bromine, but is mainly converted into 4-bromo-3:3'-diaminobenzhydrol, m. p. 110·5°, which is quite stable towards the alkali. 4:4'-Dichloro-3:3'-diaminobenzophenone (A., 1915, i, 821) is almost completely reduced to 4:4'-dichloro-3:3'-diaminobenzhydrol, m. p. 118·5°, whilst the dibromo-compound loses a fair amount of bromine and also yields 4:4'-dibromo-3:3'-diaminobenzhydrol, m. p. 126°.

The m. p.'s and b. p.'s were determined with corrected thermometers.

J. C. W.

Nitration of 4-Bromo- and 4-Chloro-benzophenones. P. J. MONTAGNE (*Ber.*, 1916, 49, 2262—2276).—When 4-bromo- and 4-chloro-benzophenones are treated with pure nitric acid in the cold, they each give three dinitro-compounds. The purpose of the present communication is to show that the main product is the 4-halogeno-3:3'-dinitrobenzophenone, that the chief by-product is the 4-halogeno-3:2'-dinitro-compound, and that the substance which is produced in the smallest amount is the 4-halogeno-3:4'-dinitro-compound. The arguments also serve to demonstrate the

positions of the substituents in 4-halogeno-2', 3', and 4'-nitrobenzophenones.

When *o*-nitrobenzyl chloride is condensed with bromobenzene and the diphenylmethane derivative is oxidised with chromic acid, 4-bromo-2'-nitrobenzophenone is produced, in crystals, m. p. 156°, b. p. 248°/11 mm. This yields 4-bromo-3:2'-dinitrobenzophenone, m. p. 150°, when treated with pure nitric acid, and this is also formed as a by-product when 4-bromo-3-nitrobenzophenone is nitrated. *m*-Nitrobenzoyl chloride condenses with bromobenzene to form 4-bromo-3'-nitrobenzophenone, m. p. 109·5°, b. p. 254°/11 mm., mixed with a little 2(?)-bromo-3'-nitrobenzophenone, m. p. 81·5°, and when this 4-bromo-3'-nitro-compound is nitrated it yields 4-bromo-3:3'-dinitrobenzophenone, m. p. 178°. On reduction with stannous chloride, this gives 4-bromo-3:3'-diaminobenzophenone, m. p. 98—99°, which may be further reduced by sodium amalgam to 3:3'-diaminobenzhydrol. 4-Bromo-4'-nitrobenzophenone (preceding abstract) yields 4-bromo-3:4'-dinitrobenzophenone on nitration, in very long, slender, pale yellow, rhombic-bipyramidal needles [*a*:*b*:*c*=1·6350:1:1·288], m. p. 134·5°, and this may also be reduced to 4-bromo-3:4'-diaminobenzophenone, m. p. 164°.

4-Chloro-2'-nitrobenzophenone, m. p. 151·5°, b. p. 236°/11 mm., from *o*-nitrobenzyl chloride and chlorobenzene, yields 4-chloro-3:2'-dinitrobenzophenone, m. p. 123·5°, on nitration. 4-Chloro-3'-nitrobenzophenone, m. p. 95·5°, b. p. 247°/13 mm., from *m*-nitrobenzoyl chloride and chlorobenzene, gives 4-chloro-3:3'-dinitrobenzophenone, m. p. 166°. (A trace of 2(?)-chloro-3'-nitrobenzophenone, m. p. 71·5°, is formed during the last Friedel-Crafts synthesis.) 4-Chloro-4'-nitrobenzophenone (preceding abstract) yields 4-chloro-3:4'-dinitrobenzophenone, m. p. 137°, and this may be reduced to 4-chloro-3:4'-diaminobenzophenone, m. p. 164·5° 3:4'-Diaminobenzhydrol, m. p. 123·75°, is formed when either 3:4'-diaminobenzophenone itself or its 4-bromo- or 4-chloro-derivative is treated with sodium amalgam.

The isolation of the above dinitrobenzophenones from the mixtures obtained by nitrating 4-chloro- and 4-bromo-benzophenones is described.

4-Bromo-3-nitrobenzophenone, from 4-bromo-3-nitrobenzoyl chloride and benzene, crystallises in transparent, pale yellow, flat needles or rhombic-bipyramidal prisms [*a*:*b*:*c*=1·5453:1:0·3847], m. p. 113·25°, b. p. 251°/16 mm., and yields 4-bromo-3:2'-dinitrobenzophenone on nitration. 4-Chloro-3-nitrobenzophenone (Maron and Fox, A., 1915, i, 265) forms pale yellow, rhombic-bipyramidal crystals [*a*:*b*:*c*=0·9363:1:0·5740], m. p. 105·5°, b. p. 235°/13 mm., and yields 4-chloro-3:2'-dinitrobenzophenone on nitration.

J. C. W.

5- and 7-Hydroxyhydrindones. K. VON AUWERS and E. HILLIGER (*Ber.*, 1916, 49, 2410—2413).—*Phenyl α*-bromopropionate is readily obtained by boiling phenol with *α*-bromopropionyl chloride, as a colourless oil, b. p. 135°/17 mm. When this is heated in small portions at a time with aluminium chloride at

140—150°, it gives good yields of 7-hydroxy- α -hydrindone, which is volatile in steam, and the para-compound, 5-hydroxy- α -hydrindone, $\text{OH}\cdot\text{C}_6\text{H}_3\langle\text{OH}_2\text{CO}\rangle\text{CH}_2$, which crystallises in glistening prisms, m. p. 183°, and forms a semicarbazone, m. p. 223°. The ortho-compound was recently described by Knake and Salkowski as a product of the dehydration of β -m-hydroxyphenylpropionic acid, but they did not decide the position of the hydroxyl group (A., 1916, i, 820).

When attempts are made to treat large quantities of the above ester in this way, 1-methylcoumaranone is obtained in varying amounts, but this can be removed by a preliminary steam distillation from a strongly alkaline solution. J. C. W.

Naphthasultam. II. Naphthasultamquinone and its Derivatives, and Ketochlorides of Tetrahydronaphthasultam. TH. ZINCKE and GRETE SCHÜRMANN (*Annalen*, 1916, 412, 78—111. Compare A., 1916, i, 426).—The analogy between 1:8-naphthasultam and α -naphthol in their behaviour with chlorine (*loc. cit.*) also extends to the quinones and their derivatives and to the ketochlorides and phenazines.

4-Amino-1:8-naphthasultam, $\text{NH}_2\cdot\text{C}_{10}\text{H}_5\langle\text{SO}_2\text{NH}\rangle$, yellow needles, is obtained by reducing sodium 1:8-naphthasultam-4-azobenzene-sulphonate, prepared in the usual way from naphthasultam and diazotised sulphanilic acid in alkaline solution, with dilute stannous chloride solution and treating the resulting hydrochloride, faintly yellow needles or leaflets with $1\text{H}_2\text{O}$, with aqueous sodium acetate. It forms a diacetyl derivative, colourless crystals, m. p. above 260° (which is easily hydrolysed to a monoacetyl derivative, colourless needles, m. p. 276°), and a sulphate, colourless crystals, which is oxidised by *N*-dichromate in the cold to 1:8-naphthasultam-4-quinone, $\text{O}\cdot\text{C}_{10}\text{H}_5\langle\text{SO}_2\text{N}\rangle$, honey-yellow or slightly brown plates and

leaflets. The quinone is odourless and has m. p. 195° (decomp.; blackening at 150°), and in general resembles α -naphthaquinone in its behaviour. It is reduced in alcoholic solution by stannous chloride to 4-hydroxy-1:8-naphthasultam, $\text{C}_{10}\text{H}_7\text{O}_3\text{NS}$, slightly yellow needles, blackening above 120° (diacetyl derivative, colourless needles, m. p. 199°), and reacts with aniline in the same solvent to form 3-anilino-1:8-naphthasultam-4-quinone,

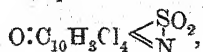
$\text{C}_{10}\text{H}_{10}\text{O}_3\text{N}_2\text{S}$, red needles, m. p. 257—260° (decomp.). The latter is converted, by heating with aqueous *N*/4-sodium hydroxide and acidifying, into 3-hydroxynaphthasultamquinone, $\text{C}_{10}\text{H}_5\text{O}_4\text{NS}$, yellow or faintly brown needles, m. p. about 230°, with previous sintering, which forms a sodium salt, red leaflets, does not yield an acetyl derivative, and is converted by aniline in warm alcoholic solution into the aniline salt, orange-red needles, in hot glacial acetic acid into the original anilino-compound. The hydroxynaphthasultamquinone is reduced by hot aqueous stannous chloride to 3:4-dihydroxy-1:8-

naphthasultam, $C_{10}H_7O_4NS$, faintly yellow needles, m. p. about 230° , with previous blackening (*triacetyl* derivative, colourless leaflets, m. p. 222°), and reacts with *o*-phenylenediamine in hot alcohol to form 1:8-*naphthasultam*-3:4-*phenazine*, $C_6H_4 \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ N \end{smallmatrix} \gg C_{10}H_4 \begin{smallmatrix} SO_2 \\ | \\ NH \end{smallmatrix}$, dark red needles, m. p. above 260° (decomp.), which is amphoteric; the *sodium* salt and the *hydrochloride*, brownish-yellow needles, have been prepared, and the *acetyl* derivative forms faintly yellow needles, m. p. about 270° .

2-*Chloro*-1:8-*naphthasultam*-4-*quinone*, $C_{10}H_4O_3NClS$, yellow leaflets, m. p. $217-218^\circ$, prepared by oxidising 2:4-dichloro-1:8-*naphthasultam* (*loc. cit.*) with hot nitric acid, D 1.32, is reduced to 2-*chloro*-4-*hydroxy*-1:8-*naphthasultam*, faintly yellow needles, m. p. about 250° (decomp.; blackening at 230°) (*acetyl* derivative, colourless needles, m. p. 186°), by stannous chloride and hot glacial acetic acid, and reacts with aniline in the same solvent to form 2-*chloro*-3-*anilinonaphthasultamquinone* (*loc. cit.*).

2:3:4-*Trichloro*-1:8-*naphthasultam* (*loc. cit.*) suspended in glacial acetic acid is oxidised by nitric acid, D 1.4, on the water-bath to 2:3-*dichloro*-1:8-*naphthasultam*-4-*quinone*, $C_{10}H_3O_3NCl_2S$, yellow needles, m. p. $216-217^\circ$, which is also easily obtained from 4-*aminonaphthasultam* in the manner described below. The *dichloroquinone*, which shows a great similarity in behaviour to 2:3-*dichloro*- α -*naphthaquinone*, yields 2-*chloro*-3-*anilinonaphthasultamquinone* by treatment with aniline in glacial acetic acid, is reduced by stannous chloride to 2:3-*dichloro*-4-*hydroxy*-1:8-*naphthasultam*, $C_{10}H_5O_3NCl_2S$, almost colourless needles, m. p. about 254° , after darkening at 220° (*sodium* salt, yellow crystals; *diacetyl* derivative, colourless needles, m. p. $205-206^\circ$), yields 2-*chloro*-1:8-*naphthasultam*-3:4-*phenazine*, $C_{16}H_8O_2N_2ClS$, reddish-brown needles with a bronze lustre, decomp. above 290° , by treatment with *o*-phenylenediamine in boiling alcohol, and is converted by 2*N*-*sodium* hydroxide into 2-*chloro*-3-*hydroxy*-1:8-*naphthasultam*-4-*quinone*, $C_{10}H_4O_4NClS$, yellow needles or prisms, which exhibits the curious property of dissolving in water or alcohol with a deep red colour, being reprecipitated unchanged by hydrochloric or nitric acid. The last-named compound is also converted into the preceding phenazine by *o*-phenylenediamine, and is reduced by stannous chloride solution and boiling glacial acetic acid to 2-*chloro*-3:4-*dihydroxy*-1:8-*naphthasultam*, $C_{10}H_6O_4NClS$, faintly yellow needles, m. p. about 256° with previous blackening, which forms a *diacetyl* derivative, colourless needles, m. p. about 285° (decomp.).

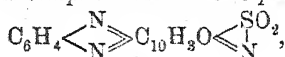
2:2:3:3-*Tetrachloro*-1:8-*naphthasultam*-4-*quinone*,



m. p. 175° , colourless leaflets or plates containing $1H_2O$, can be prepared from *naphthasultamquinone* or 2:3-*dichloronaphthasultamquinone* by moderated chlorination, but is best obtained by saturating with chlorine a suspension of 4-*aminonaphthasultam*

hydrochloride in glacial acetic and concentrated hydrochloric acids. It liberates iodine from acidified potassium iodide, yields 2:3-dichloro-4-hydroxy-1:8-naphthasultam by reduction, and is decomposed by alkali, extensively in warm aqueous solution, but in cold aqueous alcoholic solution yielding an *acid*, slender needles, which probably has the formula $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{SO}_2 \cdot \text{N} \\ \diagdown \quad \diagup \\ \text{C} \end{smallmatrix} \cdot \text{CCl} : \text{CCl}_2$.

2 : 2 - Dichloro - 3 - keto-1:8-naphthasultam-4-quinone (annexed formula), m. p. 195—196° (decomp.), almost colourless needles or faintly yellow plates with $2\text{H}_2\text{O}$, is obtained by chlorinating 2-chloro-3-hydroxy-1:8-naphthasultam-4-quinone in chloroform or glacial acetic acid. It yields chlorohydroxynaphthasultamquinone or chlorodihydroxynaphthasultam by reduction, is decomposed by boiling water or alkalis, and reacts with *o*-phenylenediamine in cold glacial acetic acid to form the 3:4-phenazine, $\text{C}_{16}\text{H}_7\text{O}_3\text{N}_3\text{Cl}_2\text{S}$, faintly red needles, m. p. 265—266° (decomp.). The formation of this azine not only shows the presence of two ortho keto-groups, but is evidence of the constitution of 2-chloro-3-hydroxy-1:8-naphthasultamquinone, and furnishes a further proof of the constitution of 3-hydroxynaphthasultamquinone and the corresponding anilino-derivative. The azine is converted by stannous chloride and glacial acetic acid into 2-chloronaphthasultam-3:4-phenazine, a suspension of which in glacial acetic acid is oxidised by warming carefully with nitric acid, D 1.4, to 2-ketodihydronaphthasultam-3:4-phenazine,



yellowish-red leaflets or needles, m. p. above 280° (decomp.). This substance is reduced by stannous chloride and hot glacial acetic acid to 2-hydroxy-1:8-naphthasultam-3:4-phenazine, $\text{C}_{16}\text{H}_9\text{O}_3\text{N}_3\text{S}$, dirty green plates, m. p. above 270° (decomp.), which forms a *diacetyl* derivative, yellow needles, m. p. about 245—246°, with previous sintering. C. S.

Preparation of Bromo- α -hydroxyanthraquinones. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 293694; from *J. Soc. Chem. Ind.*, 1916, 35, 1149).—Bromo-derivatives of α -hydroxyanthraquinones, difficult to prepare in other ways, can be obtained by the action of bromine in presence of substances capable of combining with hydrogen bromide. Thus, α -hydroxyanthraquinone yields 4-bromo- α -hydroxyanthraquinone, m. p. 197—198°, anthrarufin gives 4:8-dibromo-1:5-dihydroxyanthraquinone, and chrysazin yields 2:4:5:7-tetrabromo-1:8-dihydroxyanthraquinone. H. W.

Preparation of Transformation Products of ω -Dibromo-2-*p*-toluoylbenzoic Acid, for example, Anthraquinone-2-aldehyde. CHEMISCHE FABRIK. GRIESHEIM ELEKTRON (D.R.-P. 293981; from *J. Soc. Chem. Ind.*, 1916, 35, 1149).—Anthra-

quinone-2-aldehyde is obtained by heating ω -dibromo-2-*p*-toluoylbenzoic acid at a high temperature, or 4-aldehydobenzophenone-2'-carboxylic acid may be first formed by heating with sulphuric acid at a relatively low temperature and the action then completed at a higher temperature. Hydrolysing agents other than sulphuric acid, such as a dilute alkali solution, may be used for the first stage of the process, and any suitable dehydrating agent for the second stage.

H. W.

Preparation of Dianthraquinonylene Dioxides. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 293660; from *J. Soc. Chem. Ind.*, 1916, 35, 1151).—*o*-Nitrohydroxyanthraquinones are heated with alkaline condensing agents at a high temperature. The products, which are formed by the union of two molecules of the anthraquinone derivative with elimination of two molecules of nitrous acid, are either vat dyes or may be used in the manufacture of dyes.

H. W.

The Chemistry of the Saponins. A. W. VAN DER HAAR (*Biochem. Zeitsch.*, 1916, 76, 335—349).—The author gives a summary of his investigations (without experimental details) on the chemistry of the saponins of *Polyscia*, the crystalline α -hederin of ivy, and of saponaria- and aralea-saponins, and of senegin and digitonin. The polyscia-saponin gives on hydrolysis with 5% sulphuric acid about 33% arabinose, 37.6% dextrose, and 35% sapogenin. The latter forms rhombic crystals, m. p. 324°, contains a lactone group, but no carboxyl, hydroxyl, or methoxyl group. It has the formula $C_{26}H_{44}O_4$.

A method is indicated (without details) for the preparation of α -hederin, m. p. 256—257°, the crystalline saponin of ivy, which is insoluble in water. This substance, $C_{42}H_{66}O_{11}$, undergoes hydrolysis into the sapogenin (α -hydragenin) and arabinose and rhamnose, according to the equation $C_{42}H_{66}O_{11} + 3H_2O = C_{31}H_{50}O_4 + C_5H_{10}O_5 + C_6H_{12}O_5$. α -Hydragenin is crystalline, m. p. 325—326°, and contains a lactone and two hydroxyl groups. The same sapogenin is obtained from other saponins from ivy, which do not, however, yield the same sugars with α -hydragenin on hydrolysis. Many of the sapogenins yield on distillation with zinc dust in an atmosphere of hydrogen terpene hydrocarbons, to which the colour reaction of saponins with sulphuric acid is due.

S. B. S.

Molecular Weight of Aloin and its Products of Oxidation. E. SEEL and C. KELBER (*Ber.*, 1916, 49, 2364—2368).—The following mean values for the molecular weight of aloin are recorded: cryoscopic method: phenol, 197; ebullioscopic method: acetone, 408; ethyl alcohol, 440; ethyl acetate or acetic acid, no increment at all. These values support Léger's view that aloin has the formula $C_{21}H_{20}O_9$ or $C_{20}H_{18}O_9$ rather than $C_{16}H_{18}O_7$, which was previously assumed to be correct. Léger obtained an anthraquinone derivative and a sugar on hydrolysis (A., 1910, i, 463),

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and Seel also obtained a methyltetrahydroxyanthraquinone by oxidising aloin (A., 1901, i, 92). This gives the expected increment with boiling ethylene dibromide, and the tetra-acetate causes the expected depression in the freezing point of benzene.

J. C. W.

Anthocyanins. XI. The Anthocyanin of Red-flowering Varieties of Salvia. R. WILLSTÄTTER and E. K. BOLTON (*Annalen*, 1916, 412, 113—136).—As the investigation of the colouring matters of flowers extends, it becomes more and more evident that only a small number of sugar-free colouring matters occur in the anthocyanins, the almost infinite diversity of colour of flowers being due partly to the more or less extensive methylation of, chiefly to the nature, number, and method of union of the sugar molecules combined with, pelargonidin, cyanidin, and delphinidin (compare A., 1915, i, 282).

The scarlet-red flowers of *Salvia coccinea* and *S. splendens* contain an anthocyanin, called *salvianin*, which is a glucoside of pelargonidin, but differs in properties and behaviour from any of the known pelargonidin derivatives. The flowers are digested with ten times the weight of glacial acetic acid, and, after several days, the filtered extract is treated with ether, whereby a crude acetate is obtained, after drying, as a purplish-red powder. This is dissolved in 0.05% hydrochloric acid and treated with a saturated solution of picric acid. The crude picrate thus obtained, in amorphous, brownish-red flocks, is converted by methyl-alcoholic hydrogen chloride and ether into *salvianin chloride*, a scarlet-red powder. All attempts to prepare the chloride directly yielded only oily products. By shaking the crude anthocyanin, dissolved in about 3.5% hydrochloric acid, with a large quantity of amyl alcohol, the organic solvent removes a small amount of the anthocyanin, and from this *salvianin picrate* has been obtained in very slender, brownish-red, metallic needles. The bulk of the anthocyanin is removed from the acid mother liquor by propyl alcohol, but the picrate prepared therefrom is amorphous.

Salvianin has a complex composition and is not a simple diglucoside, since it yields by hydrolysis with boiling 20% hydrochloric acid not only pelargonidin and 2 mols. of dextrose, but also malonic acid in considerable quantity.

By keeping its solution in 6% hydrochloric acid over concentrated hydrochloric acid (renewed from time to time) in a desiccator for weeks or months, salvianin is slowly changed into a normal diglucoside, *salvinin*, and a compound, *salvin*, intermediate between this and salvianin. Salvinin forms a *chloride*, $C_{27}H_{31}O_{15}Cl$, m. p. 168° (decomp.), needles with $5H_2O$, and is isomeric with and very similar to pelargonin, but differs from it in several ways, particularly in the much stronger fluorescence of the alcoholic solution of its chloride. By hydrolysis with boiling 10—20% hydrochloric acid, salvinin yields pelargonidin and dextrose (2 mols.), but the solution obtained after the hydrolysis has proceeded for ten to twenty seconds indicates, by its colour

and its partition with amyl alcohol, the presence of an intermediate, monoglucosidic product of hydrolysis. The isolation of salvianin in quantity from the flowers is attended with not inconsiderable difficulties, and therefore the investigation of the preceding monoglucoside has not yet been attempted. However, pelargonin behaves in a similar manner, and by hydrolysis with boiling 20% hydrochloric acid for twenty to forty seconds yields a monoglucoside, *pelargonenin* (which does not appear to be identical with that from salvinin), the *chloride* of which, $C_{21}H_{21}O_{10}Cl$, forms scarlet-red needles with $2H_2O$, and is much more intensely fluorescent in alcoholic solution than is pelargonin chloride.

Salvin has not yet been fully investigated, but it appears to be different from salvianin. Its *chloride*, $C_{27}H_{27}O_{13}Cl$ (?), forms dark red prisms (from which only an oily picrate could be obtained); it is less fluorescent, and its solutions in alkalis are less blue than those of salvianin. The analytical data indicate that salvin is $C_{27}H_{26}O_{13}$ (that is, a pelargonin $-2H_2O$), and from this it would appear that two molecules, not of dextrose, but of a derivative, $C_8H_{10}O_5$, thereof, are present in the compound. Salvin exhibits a peculiarity in its partition between dilute hydrochloric acid and amyl alcohol; whilst solutions of all the diglucosides as yet examined (except rhamnoglucosides, which approximate to the monoglucosides in their behaviour) yield only a few units per cent. of their colouring matter to amyl alcohol, solutions of salvin yield more than 50% (salvianin yields almost exactly 50%). C. S.

Anthocyanins. XII. Anthocyanin of the Winter Aster (*Chrysanthemum*). R. WILLSTÄTTER and E. K. BOLTON (*Annalen*, 1916, **412**, 136—148).—A large number of scarlet-red, red, and dark red varieties of *Chrysanthemum indicum*, L., are found to contain the same cyanidin monoglucoside, which is called *chrysanthemin*, mixed in many cases with carotin and xanthophyll; in particular, the dried florets of the dark red Ruby King contain about 7% of chrysanthemin. The florets are digested for three days with glacial acetic acid (15 parts), and the chrysanthemin is precipitated by ether as the acetate, a dark violet-red powder. A solution of this in 0.5% hydrochloric acid is shaken twice with amyl alcohol and treated with a cold saturated solution of picric acid; the resulting impure picrate is converted by 10% methyl-alcoholic hydrogen chloride and ether into the impure chloride, a brownish-red, amorphous powder, and the latter is obtained in the pure, crystalline state by repeated separation from aqueous alcoholic hydrochloric acid. An alternative method of purification, based on the characteristic partition of a monoglucoside between dilute mineral acid and amyl alcohol, showed that the crude acetate obtained above contained some cyanidin and a diglucoside which is very nearly related to, if it is not identical with, cyanin.

Chrysanthemin chloride, $C_{21}H_{21}O_{11}Cl$, crystallises in clusters of acute-angled rhombic leaflets which exhibit a magnificent metallic

lustre, and are greyish-violet by transmitted light; the powder is Bordeaux-red. The substance begins to decompose at 205° and blackens without melting. It yields cyanidin chloride and dextrose (1 mol.) by hydrolysis with boiling hydrochloric acid. The *picrate* forms thin, red prisms, m. p. 165° (decomp.), sintering at 155° .

Chrysanthemin resembles the isomeric galactoside idaein in its reactions. It is also very similar to asterin (following abstract). Both these cyanidin monoglucosides exhibit the same intense ferric chloride reaction as cyanin, but differ from it in giving a violet instead of a cornflower-blue coloration with aqueous sodium carbonate.

The extraordinary dissemination of cyanidin among the anthocyanins, very frequently in the form of diglucosides, less frequently, but still not uncommonly, in the form of monoglucosides, becomes increasingly evident. Cyanin or a very similar cyanidin glucoside has often been isolated from scarlet flowers in which the presence of pelargonidin glucosides would have been expected. *Zinnia elegans* (Jacq.), *Gaillardia bicolor* (Hook), *Helenium autumnale*, L., *Gladiolus* (the scarlet varieties of which contain a pelargonidin glucoside), *Tulipa Gesneriana*, L., *Tropaeolum majus*, L., *Ribes rubrum*, L., the raspberry, and the berry of the mountain ash contain cyanidin glucosides in larger or smaller quantities, together with carotin, xanthophyll, and other pigments.

C. S.

Anthocyanins. XIII. Two Anthocyanins of the Summer Aster. R. WILLSTÄTTER and CH. L. BURDICK (*Annalen*, 1916, **412**, 149—164).—The dried florets of the purplish-red summer (china) aster (*Callistephus Chinensis*, Nees, syn. *Aster Chinensis*, L.) contain about 7.4% of a mixture of two monoglucosidic anthocyanins; the one occurring in predominant quantity is named *asterin*, the other *callistephin*.

The undried flowers were cut up and, owing to uncontrollable circumstances connected with the outbreak of the war, were digested with glacial acetic acid for a month, whereby a large part of the colouring matter in the extract was spoilt and the purification was rendered much more difficult than would have been the case had the extraction been rapidly effected. Two methods of purification are described, one involving the use of propyl alcohol and the formation of the picrates, the other utilising the lead salts. The latter, which is the better method, is as follows: The syrupy, hygroscopic mass precipitated from the acetic acid extract by ether is dissolved in 0.01% hydrochloric acid and the filtered solution is treated with lead acetate. The blue precipitate of lead salts (of the anthocyanins and of impurities) is at once extracted with glacial acetic acid, whereby a large portion of the impurities is undissolved, and the lead salts in the extract are precipitated by ether. The precipitate is shaken with propyl alcohol and 25% methyl-alcoholic hydrogen chloride, and the filtered extract is treated with ether to precipitate the chlorides of the two antho-

cyanins. These are still too impure to yield crystalline picrates, and therefore the whole process of purification is repeated. The amorphous chlorides now obtained are dissolved in 0.5% methyl-alcoholic hydrogen chloride and the filtered solution is treated with 7% hydrochloric acid and kept for five days, evaporation of methyl alcohol not being checked. The chloride which separates is submitted twice to a repetition of the process, 0.25% methyl-alcoholic hydrogen chloride being used, and pure asterin chloride is thereby obtained. Callistephin chloride is obtained by treating the mother liquors with alcohol and ether, dissolving the precipitate in methyl alcohol, and adding about 10% hydrochloric acid.

Asterin chloride, $C_{21}H_{21}O_{11}Cl$, forms bronze-brown or reddish-brown, metallic, stout prisms containing $1\frac{1}{2}H_2O$. It gives the same violet coloration with sodium carbonate and the same blue coloration with alcoholic ferric chloride as does chrysanthemin chloride (preceding abstract), but differs from this isomeric monoglucoside in being easily soluble in alcohol and in 0.5% hydrochloric acid. By hydrolysis with boiling 20% hydrochloric acid, asterin yields cyanidin and dextrose (1 mol.).

Callistephin chloride, $C_{21}H_{21}O_{10}Cl$, forms a dark brownish-red, bronze mass of hair-like needles, which appear orange-yellow under the microscope. The crystals contain $2-2\frac{1}{2}H_2O$. Although isomeric with pelargonenin (Willstätter and Bolton, this vol., i, 43), callistephin differs from it in giving a reddish-violet solution in alkalis, in forming a yellowish-red, non-fluorescent solution in alcohol, and particularly in being very easily soluble in hydrochloric acid even up to 7% concentration. Callistephin does not react with alcoholic ferric chloride, and it yields pelargonidin and dextrose (1 mol.) by hydrolysis.

C. S.

Anthocyanins. XIV. Colouring Matter of the Cherry and of the Sloe. R. WILLSTÄTTER and ERNST H. ZOLLINGER (*Annalen*, 1916, 412, 164—178).—Cyanidin glucosides occur very extensively in fruits, in yellowish-red, red, brown, and dark blue berries. Allied to idaein of the cranberry (Willstätter and Mallison, A., 1915, i, 282), *keracyanin* has been isolated from the cherry (*Prunus avium*) and *prunicyanin* from the sloe (*Prunus spinosa*). The plum (*Prunus domestica*) also contains a cyanidin glucoside, and the authors direct attention to the occurrence of a pure red colouring matter in the bluish-black skins of such fruits, and state that some explanation must be found as to how cyanidin is able to impart such deep colours to fruits.

The extraction of anthocyanins from fruit skins is comparatively simple. The dark reddish-brown skins of the cherry are separated from the rest of the fruit, freed completely from pulp by hydraulic pressure, and are extracted with glacial acetic acid without delay. The syrupy deposit obtained from the extract by the addition of ether is freed from a considerable quantity of colourless impurities by 0.5% methyl-alcoholic hydrogen chloride and ether, the solution is treated with an excess of lead acetate, the precipitated lead salts are extracted with glacial acetic acid, the extract (containing the

colouring matters, colourless impurities not being dissolved when the amount of acetic acid is suitably selected) is again precipitated with lead acetate or with ether, and the precipitate is dissolved in methyl-alcoholic hydrogen chloride. The crude chloride precipitated from the last solution by ether is purified by fractional precipitation of its solution in 0.1% methyl-alcoholic hydrogen chloride by ether. *Keracyanin chloride*, $C_{27}H_{31}O_{15}Cl$, forms red clusters of very slender needles containing $4H_2O$ (these appear yellow under the microscope), or stout prisms containing $3H_2O$ (brownish-yellow under the microscope). It resembles cyanin in the colour of its solutions in mineral acids and alcohol, but differs in giving a reddish-violet coloration in aqueous sodium carbonate and in being more soluble in dilute acids, ethyl alcohol, and amyl alcohol.

Keracyanin is a diglucoside, and by hydrolysis with boiling 20% hydrochloric acid for two and a-half to three minutes yields cyanidin, dextrose, and rhamnose.

Keracyanin and prunicyanin (see below) exhibit an important difference from other diglucosides in their partition between dilute mineral acid and amyl alcohol. Whilst cyanin and similar diglucosides yield only 1—2% of the anthocyanin to the organic solvent, keracyanin and prunicyanin resemble monoglucosides in yielding nearly 10%.

The extraction of *prunicyanin* from the skins of sloes by glacial acetic acid, the precipitation of a red syrup by methyl-alcoholic hydrogen chloride and ether, and the several processes required for the further purification of the anthocyanin are described somewhat briefly. *Prunicyanin chloride* does not crystallise readily, and therefore has not been isolated free from ash. It dissolves very easily in dilute or concentrated hydrochloric acid, develops a bluish-violet coloration with aqueous sodium carbonate, and pure blue with alcoholic ferric chloride, and yields cyanidin, rhamnose, and a hexose by hydrolysis.

Prunicyanin is comparable in many respects with mecocyanin (Willstätter and Weil, following abstract). C. S.

Anthocyanins. XV. Anthocyanin of the Pansy. R. WILLSTÄTTER and FRIEDRICH JOSEF WEIL (*Annalen*, 1916, **412**, 178—194).—Glucosides of delphinidin mono- and di-methyl ethers occur extensively in flowers and fruits, but a sugar-compound of delphinidin itself has hitherto only been found in delphinin, the anthocyanin of the larkspur (Willstätter and Mieg, A., 1915, i, 284). Since delphinin is not merely a glucoside, but yields also *p*-hydroxybenzoic acid by hydrolysis, the authors have investigated a number of blue and violet flowers with the object of finding a simple delphinidin glucoside corresponding with cyanin and pelargonin. The majority of these contained methylated delphinidins, but the flowers of the deep bluish-violet pansy (*Viola tricolor*) were found to contain a glucoside of delphinidin itself, which is called *violandin*. The dried flowers contain not less than 33% of the anthocyanin, calculated as the air-dried chloride.

The extract obtained by digesting the freshly gathered petals

with glacial acetic acid for fourteen days is treated with 10% methyl-alcoholic hydrogen chloride and ether, the precipitate is collected, washed with ether, dissolved in acidified water, and the filtered solution is treated with 4% hydrochloric acid, whereby pure *violanan chloride* is obtained. A remarkably pure crude product is obtained by rapidly extracting the flowers with 2% methyl-alcoholic hydrogen chloride and treating the filtered extract with ether. Violanan chloride forms bluish-violet aggregates of crystals with a green, metallic lustre; by careful crystallisation, six-sided and tetrahedral plates can be obtained. Violanan resembles delphinidin in the colour of its solutions, but differs therefrom in forming a colourless carbinol (ψ -base) in dilute solution (*loc. cit.*). It forms pure blue solutions in alkali hydroxide or carbonate solutions, in disodium hydrogen phosphate solution, and with alcoholic ferric chloride or alum. By hydrolysis with boiling 20% hydrochloric acid, violanan chloride yields delphinidin, rhamnose, and dextrose, but the latter two are not obtained in molecular quantities. On this account the composition of violanan has not yet been definitely settled; it appears to be $C_{27}H_{28}O_{15}$, that is, delphinidin rhamnoglucoside, $(C_{27}H_{30}O_{16} - 1H_2O)$.

Similarly to the other rhamnoglucosides, keracyanin and prunicyanin (preceding abstract), violanan resembles a monoglucoside in its partition between dilute acid and amyl alcohol. Fractional extraction with amyl alcohol proved that violanan is not a mixture of two or more constituents.

Violanan picrate forms cherry-red, felted needles which appear blue under the microscope; when dried, it forms a copper-red mass with a metallic lustre.

The identification of delphinidin and its purification are made somewhat difficult owing to its tendency to form hydrates of different appearance and widely varying solubility. Four of these, with 1, 1½, 2, and 4H₂O respectively, are described, and the conditions for their preparation given in detail. C. S.

Anthocyanins. XVI. Colouring Matter of the Grape and of the Bilberry. II. R. WILLSTÄTTER and ERNST H. ZOLLINGER (*Annalen*, 1916, 412, 195—216. Compare A., 1915, i, 285).—The sugar present in myrtillin has been recognised as galactose (phenylmethylhydrazone, m. p. 188—189°). Myrtillidin yields phloroglucinol when it is heated with 75% potassium hydroxide at 110° for a few minutes. This fact, taken in conjunction with the intense ferric chloride reaction of myrtillidin, shows that the anthocyanidin (which is a delphinidin monomethyl ether) must have its methoxyl group in position 3 or 3'.

Grapes from different sources are shown in the following way to contain, in addition to the monoglucoside oenin, more or less of the sugar-free anthocyanidin, oenidin; it is very probable that a few units per cent. of a diglucoside are also present in some varieties of grapes. The grapes are pressed, and the skins, after being soaked in boiling water for a short time, are ground with sand and rapidly extracted with dilute aqueous hydrochloric acid.

The extract is shaken with amyl alcohol. The alcoholic solution, even after repeated washing with dilute acid, retains a small (in some cases a considerable) amount of colouring matter, which must therefore be the anthocyanidin. This is the case with grapes from North Italy, and also with indigenous greenhouse grapes.

The partition of anthocyanins between dilute mineral acid and amyl alcohol free from pyridine is of great analytical importance, not only for the preceding reason, the testing of the individuality of an anthocyanin, but also because it indicates whether an anthocyanin is a monoglucoside or a diglucoside. The acid must be sufficiently concentrated to prevent conversion of the coloured chloride into the colourless carbinol, and yet must be dilute enough to dissolve the chloride readily. The authors recommend 0.5% hydrochloric acid. The solutions in this solvent must be very dilute on account of the limited solubility of the colouring matter in amyl alcohol. The intensity of the colour of the amyl-alcoholic solution is compared with that of a freshly prepared, standard solution of the anthocyanin chloride. Two successive extractions with amyl alcohol are made, and the fraction of the anthocyanin in the extracts (called the "partition number") should be the same in both cases. By employing this method, the authors have prepared pure oenin chloride from Italian grapes. It forms dark prisms with a green metallic lustre, containing $4\text{H}_2\text{O}$ (compare *loc. cit.*).

The effect of tannins on the colour reactions of certain anthocyanins (cyanin, oenin, and myrtillin) is described.

The anthocyanin in the berries of the wild vine (*Ampelopsis quinquefolia* Michx.; *Vitis hederacea* Ehrh.) is present mainly in the skins, although not so completely as in the case of the cultivated vine. The skins are pressed between filter-paper and extracted with glacial acetic acid. The violet powder precipitated from the extract by ether is dissolved in methyl-alcoholic hydrogen chloride, and the crude chloride thrown out by ether is dissolved in 0.1% hydrochloric acid, and powdered picric acid is added to the solution. The *picrate* of the anthocyanin, which is called *ampelopsin*, is obtained in crimson red, felted needles. The *picrate* is converted by 3–4% methyl-alcoholic hydrogen chloride and ether into the nearly pure, amorphous chloride, which is obtained crystalline by further purification by aqueous-alcoholic hydrochloric acid. *Ampelopsin chloride*, $\text{C}_{22}\text{H}_{29}\text{O}_{10}\text{Cl}$, crystallises in dark brownish-green, glistening prisms resembling those of oenin chloride, and yields dextrose (1 mol.) and *ampelopsidin* by hydrolysis with boiling 20% hydrochloric acid.

The skins of the berries of *Vitis riparia*, treated in the manner described above, yield a crystalline monoglucosidic *anthocyanin chloride*, $\text{C}_{22}\text{H}_{29}\text{O}_{10}\text{Cl}$ (to which a specific name has not yet been given). This anthocyanin differs from ampelopsin in giving a pronounced, but transient, violet coloration with aqueous ferric chloride and a stable blue solution with alcoholic ferric chloride; ampelopsin develops a faint coloration with the former reagent and a fine violet with the latter.

C. S.

Anthocyanins. XVII. The Colouring Matter of the Petunia. R. WILLSTÄTTER and CH. L. BURDICK (*Annalen*, 1916, 412, 217—230).—The widely cultivated “Karlsruher Rathaus” petunia (*P. hybrida hort.*) contains an individual, well-crystallised anthocyanin, *petunin*, which is a diglucoside of *petunidin*, a new delphinidin monomethyl ether similar to myrtillidin. The flowers, which in the dried state contain 15.4% of hydrated petunin chloride, are rapidly extracted with glacial acetic acid; the purification by means of ether, methyl-alcoholic hydrogen chloride, etc., follows very much along the usual lines. *Petunin chloride*, $C_{28}H_{33}O_{17}Cl$, forms elongated plates containing $2H_2O$, m. p. about 178° , which appear a magnificent violet colour by transmitted light and have a copper lustre by reflected light. Its dilute aqueous solution loses its reddish-violet colour in the course of time, and then contains the colourless ψ -base. Petunin chloride is very easily soluble in methyl alcohol, develops a violet coloration with methyl-alcoholic (not ethyl-alcoholic) ferric chloride, and yields with aqueous sodium carbonate a solution the violet colour of which soon becomes blue.

Petunin is not precipitated as the picrate by picric acid.

By boiling with 20% hydrochloric acid, petunin chloride yields dextrose (2 mols.) and *petunidin chloride*, $C_{16}H_{13}O_7Cl$, which yields several hydrates having different crystalline forms and solubility. Petunidin closely resembles myrtillidin in its reactions, but shows the following two characteristic differences. Petunidin which has been washed with alcohol is insoluble in 0.5% hydrochloric acid, whilst myrtillidin after similar treatment is easily soluble. Petunidin crystallised from hydrochloric acid is insoluble in 3% hydrochloric acid, whilst myrtillidin is appreciably soluble.

Petunidin yields delphinidin by demethylation with hydriodic acid in the presence of phenol, and phloroglucinol by heating with very concentrated aqueous potassium hydroxide at 140° . C. S.

Anthocyanins. XVIII. Colouring Matter of the Poppy. I. R. WILLSTÄTTER and FRIEDRICH WEIL (*Annalen*, 1916, 412, 231—251).—An investigation of the colouring matters of various kinds of poppy has been undertaken since preliminary experiments have indicated that the isolation of several new anthocyanidins (fundamental substances different from cyanidin, pelargonidin, and delphinidin) may be expected. At present, owing to the war, only one investigation has been finished, and this has not produced a new anthocyanidin.

The flowers of the corn-poppy (*Papaver Rhoeas*) contain a mixture of the diglucosides of two anthocyanidins. The predominating anthocyanin is a cyanidin derivative, and is named *meocyanin*. The other anthocyanin resembles the delphinidin glucosides, but the anthocyanidin in it has not been obtained in the pure state.

The freshly gathered flowers are treated with glacial acetic acid, and the extract is treated with 10% methyl-alcoholic hydrogen chloride and ether. The product is further purified (1) by pre-

precipitation from hydrochloric acid solution by alcohol to remove slimy impurities; (2) solution in alcohol to remove the accompanying anthocyanin and inorganic salts; (3) separation from the alcoholic solution to remove the more easily soluble, less pure portions; and (4) fractional precipitation by glacial acetic acid from aqueous solution containing hydrochloric acid.

Mecocyanin chloride, $C_{37}H_{31}O_{16}Cl$, is obtained by the last operation in dark red, crystalline grains. It is easily soluble in water; the dilute solution becomes colourless owing to carbinol formation. It differs from cyanin and other cyanidin glucosides in its extreme solubility in hydrochloric acid (0.01% to 10% or more). Mecocyanin resembles cyanin in the colours of its solutions in acids and in alcohol, but differs in giving a bluish-violet solution in aqueous sodium carbonate. The salts of mecocyanin are very soluble except the *ferrocyanide*, which crystallises in almost black, felted needles with a green, metallic lustre.

Mecocyanin yields cyanidin chloride and dextrose (2 mols.) by hydrolysis with boiling 20% hydrochloric acid. By digesting mecocyanin with concentrated hydrochloric acid for a few hours or with 20% hydrochloric acid for a few days at the ordinary temperature, it is converted into a monoglucoside which is shown to be identical with chrysanthemin (Willstätter and Bolton, this vol., i, 43). C. S.

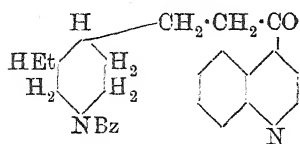
Preparation of α -Methylcoumarones. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 293956; from *J. Soc. Chem. Ind.*, 1916, 35, 1180; addition to D.R.-P., 279864, A., 1915, i, 707). — α -Methylcoumarones, suitable for pharmaceutical purposes and for use in perfumery, are formed by the action of alkalis on α -halogeno- α -allylphenols. H. W.

Degradation of the Cinchona-alkaloids. I. ADOLF KAUFMANN, ERNST ROTHLIN, and PAUL BRUNNSCHWEILER (*Ber.*, 1916, 49, 2299—2310).—Recent researches have shown that meroquinine or the product of its hydrogenation, cincholeupone, are common to all the cinchona-alkaloids, being combined in these with cinchonic or quinic acids. Derivatives of the latter acids are now easily prepared, and therefore if the former acids could be isolated readily from the less valuable alkaloids it might be possible to synthesise from them the more important bases. The difficulty has so far been the production of meroquinine or cincholeupone in quantity, but improved methods are now described.

Starting with cinchotine, which can be obtained in large amounts by hydrogenating the vinyl chain in cinchonine, this is transformed by treatment with acetic acid into cinchotoxine; the benzoyl derivative of this is converted into the oximino-compound, and this is broken down by means of *p*-toluenesulphonyl chloride into cinchonic acid and benzoylcincholeuponitrile, which yields cincholeupone on hydrolysis. The various stages are easily carried through.

New, systematic names are proposed for the alkaloids, the principal novelty being the adoption of Pasteur's nomenclature for the "toxines"; thus, "quinotoxine" becomes "quinicine." The new names are given in brackets.

Dihydrocinchonine (cinchotine) hydrochloride is boiled with sodium acetate and 50% acetic acid for several hours, the product is rendered alkaline, and the cinchotoxine (cinchoticine) is extracted with ether and converted into *benzoylcinchoticine* (annexed



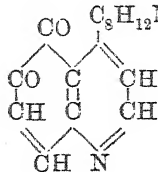
formula), which crystallises in groups of white needles, m. p. 124°. This forms an oily *dimethosulphate*, the *picrate* of which has m. p. 152—154°. When the benzoylcinchoticine is boiled with chromic acid in glacial acetic acid solution and the product is diluted and extracted with ether, cinchonic acid is found in the aqueous portion and benzoylcincholeupone, with much unchanged material, in the extract. The two acids are isolated first as their copper salts. The dimethosulphate undergoes a different fission on oxidation with permanganate. The quinoline nucleus is removed as formyl-methylantranilic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{COH}$, whilst the piperidine nucleus is apparently preserved in benzoylhomocincholeupone (1-benzoyl-5-ethylpiperidine-4-propionic acid). This could not be purified, but was transformed by hydrolysis and esterification into ethyl 5-ethylpiperidine-4-propionate, b. p. 136°/11 mm.

The *isonitrosobenzoylcinchoticine* is readily obtained by the action of amyl nitrite in the presence of sodium ethoxide in white needles, m. p. 175—177°, and is quantitatively transformed into cinchonic acid and *benzoylcincholeupononitrile* (1-benzoyl-5-ethylpiperidine-4-acetonitrile), b. p. 160—165°/mercury vacuum, when a solution in 5% sodium hydroxide is shaken with *p*-toluenesulphonyl chloride at 45°. The nitrile is conveniently hydrolysed to cincholeupone (5-ethylpiperidineacetic acid) and benzoic acid by warming with 70% sulphuric acid.

J. C. W.

Thalleioquinine. A. CHRISTENSEN (*Ber. Deut. pharm. Ges.*, 1916, 26, 249—261. Compare A., 1915, i, 711).—In extension of his investigation on the action of chlorine on quinine, the author has turned his attention to the nature of the green substance, thalleioquinine, of which a solution is obtained when a quinine salt is treated successively with solutions of chlorine and ammonia. The thalleioquinine prepared by the action of aqueous ammonia on the nitrate of the so-called 5-dichloro-6-ketocinchonine hydroxychloride (*loc. cit.*) was not pure, but appeared to contain some of the unaltered nitrate. Better results were obtained with the more soluble nitrate of the base derived from chlorohydroquinine (*loc. cit.*), which on careful treatment with aqueous ammonia gave a thalleioquinine of the composition $\text{C}_{19}\text{H}_{21}\text{O}_3\text{N}_2\text{Cl}_2\text{NH}_3$; the molecule of ammonia is removable by keeping over phosphoric oxide in a vacuum, and the remaining substance probably has the structure of chloro-5:6-diketohydrocinchonine. The structure of the

thalleioquinine derived from quinine by the well-known chlorine-ammonia test is therefore probably that of chloro-5:6-diketo-



hydroxycinchonine (annexed formula), also with the addition of a loosely bound molecule of ammonia. Evidence is adduced as to the ease with which a chlorine atom in the 5-position adjacent to a hydr-

oxyl group in the 6-position of the quinoline nucleus of such compounds as the above is eliminated by the action of ammonia, the concurrent action of an oxidising substance causing the formation of a $\cdot\text{CO}\cdot\text{CO}\cdot$ group. On this account, it is possible to prepare thalleioquinine analogues from 5-chloro-6-hydroxycinchonine hydrochloride by the action of silver sulphate or nitrate in the presence of potassium persulphate or lead dioxide in a dilute acid medium, with the subsequent addition of aqueous ammonia. In these reactions, the silver salt serves to effect the removal of the chlorine.

In an analogous manner, 5-chloro-6-hydroxyquinoline has been shown to be oxidisable to a compound which gives a green coloration with aqueous ammonia (Mathëus, A., 1888, 965), and it is now demonstrated that the oxidation may be effected with various other oxidising agents, such as lead dioxide, chlorine water, or a mixture of silver sulphate and potassium persulphate, in each case in the presence of dilute sulphuric acid.

D. F. T.

Degradation of Scopoline. K. HESS (*Ber.*, 1916, 49, 2337—2339. Compare A., 1916, i, 285).—A claim for priority against E. Schmidt (*ibid.*).

J. C. W.

Fractionation of the Phosphotungstic Acid Precipitate with Acetone for the Preparation of Vitamine from Yeast.

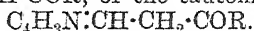
CASIMIR FUNK (*Biochem. Bull.*, 1916, 5, 1—16; from *Physiol. Abstr.*, 1916, 1, 42).—The phosphotungstates from an alcoholic yeast extract are largely soluble in acetone; the bulk of the vitamine is, however, contained in a small fraction insoluble in acetone. Phosphotungstates may be decomposed with lead acetate, instead of barium hydroxide; this new method yields clear solutions, facilitates purification, and avoids the use of alkali.

G. B.

The Condensation of Pyrrole-2-aldehyde with Ketones.

EVA LUBRZYNSKA (*T.*, 1916, 109, 1118—1120).—Although it has been suggested (Angeli and Marchetti, A., 1909, i, 12; Alessandri, A., 1915, i, 452, 988) that pyrrole-2-aldehyde exists in the hydroxymethylene form, the fact that the substance yields the usual condensation products of an aldehyde with *p*-nitrophenylhydrazine, hydroxylamine, and semicarbazide (Bamberger and Djerdjian, A., 1900, i, 309; Tschelincev and Terentjev, A., 1915, i, 452) proves that it can react in the aldehydic form. As an extension of the present knowledge of the reactions of the substance, the author has

effected the condensation of pyrrole-2-aldehyde in the presence of alkali with methyl ethyl ketone, yielding a pale yellow *substance*, $C_9H_{11}ON$; with acetophenone giving a yellow *substance*, $C_{13}H_{11}ON$, and with acetone producing a yellow *substance*, C_8H_9ON ; the general structure of these products is probably represented by the formula $C_4H_4N \cdot CH:CH \cdot COR$, or the tautomeric



In the case of acetone a very small quantity of an intense orange-coloured *substance* was also obtained, possibly of the structure $CO(CH:CH \cdot C_4H_4N)_2$. For experimental details see original.

D. F. T.

Preparation of Mononitrocarbazoles. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 294016; from *J. Soc. Chem. Ind.*, 1916, **35**, 1149).—Carbazole or an *N*-alkyl, *N*-aryl, or halogen derivative is dissolved or suspended in an inert medium immiscible with water and treated with nitric acid.

H. W.

Condensation of Thiobarbituric Acid with Aromatic Aldehydes. ARTHUR W. DOX and G. P. PLAISANCE (*J. Amer. Chem. Soc.*, 1916, **38**, 2164—2166. Compare this vol., ii, 53).—The authors have condensed thiobarbituric acid in solution in 12% hydrochloric acid with a number of aromatic aldehydes in similar solution at the ordinary temperature. The following compounds are described:—

Benzylidenemalonylthiocarbamide, a lemon-yellow precipitate, readily soluble in pyridine and alkali hydroxides.

o-*Hydroxybenzylidenemalonylthiocarbamide*, a bright vermilion precipitate, giving with dilute ammonia or alkali hydroxides a deep wine-red colour, which rapidly disappears.

o-*Nitrobenzylidenemalonylthiocarbamide*, a greenish-yellow product.

p-*Methoxybenzylidenemalonylthiocarbamide*, a deep yellow precipitate.

4-*Hydroxy-3-methoxybenzylidenemalonylthiocarbamide*, brilliant, orange-coloured precipitate, giving with alkali hydroxides a mahogany-red solution, the colour of which rapidly disappears.

3:4-*Methylenedioxybenzylidenemalonylthiocarbamide*, a bright orange-coloured precipitate.

3:4-*Dihydroxyphthalylidenemalonylthiocarbamide*, a reddish-brown precipitate, soluble in alkali hydroxides to a mahogany-red solution.

Cinnamylidenemalonylthiocarbamide, a bright orange-red precipitate.

None of these compounds could be melted without decomposition, the decomposition temperatures not being sharp. The condensation products from the three aldehydes having a hydroxyl group in the benzene nucleus all gave a deep red coloration with alkali hydroxides, the others remaining colourless. All the condensation products were soluble in these alkalis. The reaction was in every case practically quantitative.

Three aliphatic aldehydes were tried—formaldehyde, acetaldehyde, and citral—but failed to react under the above conditions.

W. G.

Preparation of Amino-derivatives of 2-Phenylquinoline-4-carboxylic Acid and its Substitution Products. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 294159, addition to D.R.-P., 287804; from *J. Soc. Chem. Ind.*, 1916, **35**, 1180).—Amino-derivatives of 2-phenylquinoline-4-carboxylic acid or its substitution products are prepared by condensing mono-acyl derivatives of phenylenediamines, their homologues, or substitution products with benzaldehyde, its homologues, or substitution products, and pyruvic acid, and saponifying the resulting *N*-acyl compounds (compare A., 1916, i, 333, 334).

H. W.

The 2-Thio-3-aryl-5:5-dimethylhydantoins. J. R. BAILEY and A. T. McPHERSON (*J. Amer. Chem. Soc.*, 1916, **38**, 2523—2527).—The authors have repeated Stelzner's work on the preparation of 2-thio-3-*o*-tolyl-5:5-dimethylhydantoin (compare A., 1892, 149) and certain of its derivatives, and, as in the case of other similarly constituted thiohydantoins (compare Bailey and Randolph, A., 1908, i, 741, 742), have obtained compounds differing considerably in their m. p. from the figures given by Stelzner. The authors find that 2-thio-3-*o*-tolyl-5:5-dimethylhydantoin has m. p. 195.5°, and when desulphurised gives 3-*o*-tolyl-5:5-dimethylhydantoin, thin, prismatic plates, m. p. 172°. The thiohydantoin gives a *methyl ether*, m. p. 75°, which forms a *picrate*, m. p. 152°, a *platinichloride*, m. p. 220°, and a *sulphate*, m. p. 196°. *o*-Tolylthio-urethane (compare Liebermann and Natanson, A., 1881, 45) was also obtained in a crystalline state, m. p. 37°.

W. G.

Organic Periodides. II. Periodides of Antipyrine, Iodoantipyrine, and Pyramidone. W. O. EMERY and S. PALKIN (*J. Amer. Chem. Soc.*, 1916, **38**, 2166—2181. Compare Kippenberger, A., 1897, ii, 292, and Scholtz, A., 1899, ii, 390, 584; 1900, ii, 638).—The authors have succeeded in isolating periodides of antipyrine, iodoantipyrine, and pyramidone in a crystalline form. Preliminary examination of the behaviour of antipyrine towards a solution of iodine in potassium iodide gave results confirming those of Scholtz (*loc. cit.*), as opposed to those of Kippenberger (*loc. cit.*). When a solution of iodine in aqueous potassium iodide is added to an acidified aqueous solution of antipyrine a tarry product is obtained in every case. The amount of iodine removed from solutions varies inversely with the amount of mineral acid present and directly with the amount of iodine added for a given weight of antipyrine. The limit of iodine removable is approximately four atoms for each molecule of antipyrine. A certain amount of the iodine is substituted in the molecule, the amount varying with the concentration of the iodine and the mineral acid.

From the tars precipitated under the above conditions it is possible by use of suitable solvents to isolate crystalline periodides,

but these are best prepared by the admixture of antipyrine, hydriodic acid, and iodine in organic solvents, the most satisfactory being alcohol, ether, or ethyl acetate. By varying the quantities of the three substances used the following compounds were obtained.

Triantipyrine dihydriodotettriiodide, $(C_{11}H_{12}ON_2)_3 \cdot (HI, I_2)_2$, steely-blue, needle-like prisms, D 1.91, m. p. 79—80°, having a metallic lustre. They were odourless when dry and quite stable in the air.

Diantipyrine hydriododi-iodide, $(C_{11}H_{12}ON_2)_2 \cdot HI, I_2$, slender, glistening, ruby-red needles, m. p. 96—97°.

Iodoantipyrine was readily prepared by adding a $N/10$ -solution of iodine in potassium iodide to a solution of 2 grams of antipyrine and 1 gram of sodium hydrogen carbonate in water at 50° until a faint yellow colour persisted after stirring. On cooling, colourless needles of iodoantipyrine separated, and from it, by the above methods, the following periodides were prepared:

Di-iodoantipyrine hydriododi-iodide, $(C_{11}H_{11}ON_2I)_2 \cdot HI, I_2$, ruby-red needles, m. p. 124—125°.

Di-iodoantipyrine hydriodotettriiodide, $(C_{11}H_{11}ON_2I)_2 \cdot HI, I_4$, chocolate-coloured prisms, difficult to purify.

Di-iodoantipyrine hydriodohexiiodide, $(C_{11}H_{11}ON_2I)_2 \cdot HI, I_6$, dark green, glistening, acicular prisms, m. p. 97—98°.

Two crystalline periodides were prepared from pyramidone hydriiodide in a similar manner. Pyramidone hydriododi-iodide, $C_{13}H_{17}ON_3 \cdot HI, I_2$, ruby-red needles, m. p. 190° (compare Cousin, A., 1909, i, 190). *Pyramidone hydriodotri-iodide*, $C_{13}H_{17}ON_3 \cdot HI, I_3$, green, glistening leaflets, m. p. 155—156°.

Both these periodides can be prepared directly from pyramidone itself by dissolving the components in alcohol and allowing the resulting additive product to separate slowly by crystallisation.

W. G.

The cycloPentadiene Series. IV. The Formation of cycloPentadienedihydropyridazines. WILLIAM J. HALE (*J. Amer. Chem. Soc.*, 1916, **38**, 2535—2545).—The monohydrazones and phenylhydrazones of 5-nitro-2:3-diacetylcyclopentadiene and the corresponding dibenzoyl compound have been shown to be unstable (compare A., 1912, i, 994; 1913, i, 184, 369), undergoing intramolecular condensation with the production of coloured compounds. These have now been studied, and their products of oxidation determined.

When 5-nitro-2:3-diacetylcyclopentadiene in solution in aqueous sodium carbonate is treated with hydrazine sulphate, a yellow precipitate of the hydrazone is formed at first, and then redissolves, and finally an orange-red precipitate of 6-nitro-1:4-dimethyl-

cyclopentadienedihydropyridazine, $NO_2 \cdot C \begin{smallmatrix} \text{CH} \cdot \text{C} \cdot \text{CMe} \cdot \text{NH} \\ \text{CH} \cdot \text{C} \cdot \text{CMe} \cdot \text{N} \end{smallmatrix}$, red

prisms, m. p. 240—245° (decomp.), is obtained. When this substance is dissolved in just sufficient aqueous potassium hydroxide to form the potassium salt and oxidised with 4% potassium permanganate on a water-bath, it yields 3:6-dimethylpyridazine-4:5-di-

carboxylic acid, $C_4N_2Me_2(CO_2H)_2$, colourless prisms, m. p. 226—228° (decomp.). It gives a white, insoluble *silver salt*.

If an excess of phenylhydrazine is added to an alcoholic solution of 5-nitro-2:3-diacetylcyclopentadiene and the mixture warmed for an hour, 6-nitro-2-phenyl-1:4-dimethylcyclopentadiene-

dihydropyridazine, $NO_2-C \begin{smallmatrix} \text{CH} \cdot C : CMe \cdot NPh \\ | \\ \text{CH} \cdot C : CMe \cdot N \end{smallmatrix}$, yellow needles, m. p.

193°, is obtained. This compound, when oxidised in acetone solution with potassium permanganate in the same solvent, yields 4-keto-1-phenyl-3:6-dimethyl-1:4-dihydropyridazine-5-carboxylic acid, colourless needles, m. p. 220°, and oxalic acid.

When 5-nitro-2:3-dibenzoylcyclopentadiene in benzene-alcohol solution is warmed with an excess of hydrazine hydrate in alcoholic solution for a few hours, 6-nitro-1:4-diphenylcyclopentadiene-dihydropyridazine, orange-red prisms, m. p. 275—280° (decomp.), is obtained. The original dibenzoyl compound, when digested in hot benzene solution with an excess of phenylhydrazine for eight hours, yields 6-nitro-1:2:4-triphenylcyclopentadienedihydropyridazine, orange-red prisms, m. p. 287°. These two compounds were not submitted to the oxidising action of potassium permanganate.

W. G.

Manufacture of Anthracene Dyestuffs [Alkylated Pyrazole anthrone Yellow]. CHEMISCHE FABRIK. GRIESHEIM ELEKTRON (Brit. Pat., 14103; from *J. Soc. Chem. Ind.*, 1916, **35**, 1104).—Pyrazole-anthrone-yellow (A., 1913, i, 533) or an alkali salt is treated with an alkylating or arylating agent. Thus, pyrazoleanthrone-yellow (1 part) in the form of a paste is digested with 5% potassium hydroxide solution until completely converted into the violet potassium salt, the solution diluted until it contains 3—5% potassium hydroxide, and the salt drained as far as possible; the paste obtained is heated with benzyl chloride (1 or 2 parts) in a closed vessel at 100° for three hours, and the product is diluted with alcohol, filtered, and the residue washed with alcohol. The *monobenzyl* derivative produced gives with hyposulphite a blue vat, from which cotton is dyed scarlet shades. When the benzyl derivative (38 parts) in the form of the dried potassium salt is heated, with stirring, in an autoclave for one hour at 120° with methyl toluene-*p*-sulphonate (120 parts), the *benzylmethyl* derivative is obtained; this product dyes cotton an excellent fast red.

H. W.

Autoxidation of Benzaldehydephenylhydrazone in Alcohol. M. BUSCH and HERM. KUNDE (Ber., 1916, **49**, 2345—2358. Compare A., 1915, i, 307).—Under the influence of air and light, alcoholic solutions of benzaldehydephenylhydrazone become red, owing to oxidation. Stobbe and Nowak (A., 1913, i, 1200) isolated from such a solution diphenyldibenzylidenedihydro-tetrazone, benzaldehyde, and benzoic acid, but it is now shown that the reaction is a very complicated one, and the existence of

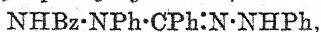
the eight or nine products which the authors have obtained can be referred back very largely to the participation of the primary peroxide.

A suspension of benzaldehydephenylhydrazone (40 grams) in alcohol (600 c.c.) and glacial acetic acid (5 c.c.) is shaken with oxygen for about a day until no more gas is absorbed and solution is complete. A trace of diphenyldibenzylidenehydrotetrazone, $N_2Ph_2(N:N:CHPh)_2$, usually separates towards the end in iridescent needles; these are removed, and the filtrate left to evaporate. In a day or two yellow needles (*A*) are deposited, followed by stout prisms (*B*) during the next few days. The mother liquor then becomes oily, and after about a week deposits a yellow powder (*C*), and contains much benzaldehyde and benzoic acid. After removing the acid by means of sodium carbonate solution, the dark mass which remains can be made to yield a further solid (*D*). The effect of temperature and of other acids (for example, tartaric) on the nature of the products is briefly mentioned.

The substance *A* is pure *benzoyldiphenylbenzylidenehydrotetrazone*, $NHBz \cdot NPh \cdot NPh \cdot N:CHPh$, and crystallises in yellow needles, m. p. 105—106°. It may be reduced by means of zinc dust and acetic acid to benzaldehydephenylhydrazone and β -benzoylphenylhydrazine, and it is easily prepared by the condensation of benzaldehydephenylhydrazone with benzoylazo-benzene. Inasmuch as the peroxide of benzaldehydephenylhydrazone suffers transformation into benzoylphenylhydrazine and benzoylazobenzene, the production of substance *A* can easily be accounted for. The yield of it is also considerably enhanced if β -benzoylphenylhydrazine is added to the alcoholic suspension at the outset.

Solutions of *A* in alcohol or benzene become dark red on boiling, especially in the presence of ammonia, owing to the production of *benzoylformazylbenzene*, $NPhBz \cdot N:CPh \cdot N:NPh$, which crystallises in brilliant, very dark red prisms, m. p. 139°, and sometimes in orange-red prisms, m. p. 146—147°. The two hydrogen atoms which are lost apparently go to the production of oily by-products. The compound may be reduced to a hydrazo-compound by mild agents, but zinc dust and sulphuric acid, on warming, give rise to the formation of α - and β -benzoylphenylhydrazines. Alcoholic hydrogen chloride causes a vigorous evolution of nitrogen and forms ethyl benzoate and α -benzoylphenylhydrazine hydrochloride.

Substance *B* is an isomeride of *A*, namely, *benzoylphenylhydrazinobenzaldehydephenylhydrazone*,

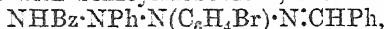


and is obtained when the latter is left in a mixture of alcohol and acetic acid for about a week. It crystallises in almost colourless needles or columns, m. p. 177°, but combines readily with alcohol (stout leaflets) or benzene (white needles). It forms a *nitroso*-compound, brilliant, colourless, stout crystals, m. p. 114°, and may

be hydrolysed by dilute sulphuric acid to phenylhydrazine and $\alpha\beta$ -dibenzoylphenylhydrazine.

Compound *C* is *benzeneazodiphenylmethane*, $\text{NPh}\cdot\text{N}\cdot\text{CHPh}_2$; it forms deep lemon-yellow leaflets or needles, m. p. $74-75^\circ$, and changes into substance *D*, which is benzophenonephenylhydrazone, when an ethereal solution is left in contact with a trace of hydrogen chloride.

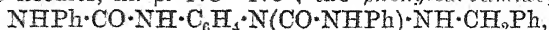
Some other benzoyldiphenylbenzylidenehydrotetrazones have been prepared; by the condensation of benzaldehyde-*p*-bromophenylhydrazone with benzoylazobenzene, the compound,



is formed, in pale yellow needles, m. p. $97-98^\circ$; benzaldehydephenylhydrazone and benzoylazo-*p*-bromobenzene yield the *isomeride*, $\text{NHBz}\cdot\text{N}(\text{C}_6\text{H}_4\text{Br})\cdot\text{NPh}\cdot\text{N}\cdot\text{CHPh}$, m. p. $109-110^\circ$, whilst *benzoyl-di-p-bromophenylbenzylidenehydrotetrazone* crystallises in canary-yellow leaflets, m. p. $120-121^\circ$, and changes into the *formazyl* compound, garnet-red leaflets, m. p. 151° , on warming with benzene or alcohol and a trace of ammonia. J. C. W.

Aminohydrazines. III. *o*-Aminophenyl- β -benzylhydrazine.

HARTWIG FRANZEN and BERTHOLD VON FÜRST (*Annalen*, 1916, **412**, 14-35. Compare A., 1907, i, 321; 1914, i, 206).—The remarkable property of *o*- and *p*-aminophenylbenzylidenehydrazines (benzaldehyde-*o*- and *p*-aminophenylhydrazones) of yielding the phenylenediamine, ammonia, and benzaldehyde by treatment with hot acids may be due to the amino-group, to the double linking, or to both. These alternatives have now been investigated. All attempts to prepare *p*-aminophenyl- β -benzylhydrazine were unsuccessful. Benzaldehyde-*o*-aminophenylhydrazone, however, which reacts with phenylthiocarbimide in boiling alcohol to form the *phenylthiocarbamide*, $\text{CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, pale yellow needles, m. p. $218-220^\circ$, with benzoyl chloride in cold pyridine to form the *benzoyl* derivative, $\text{CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NHBz}$, colourless leaflets, m. p. $190-193^\circ$, and with boiling alcoholic hydrogen chloride to form 2-phenylbenziminazole quantitatively, is reduced in boiling alcoholic solution by 3% sodium amalgam, yielding *o*-aminophenyl- β -benzylhydrazine, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, which is obtained in needles, m. p. $62-63^\circ$, to a turbid, yellow liquid clarifying at 80° , or after repeated crystallisation in citron-yellow needles, m. p. 73° (sharp). The substance decomposes within a few hours, develops in alcoholic solution an intense Bordeaux-red coloration with a few drops of mineral acid, and forms a *hydrochloride*, $\text{C}_{13}\text{H}_{15}\text{N}_3\cdot 2\text{HCl}$, violet-red powder, m. p. $201-202^\circ$ (from an alcoholic solution of which the yellow hydrazine is regenerated by ammonia at -10°), the *phenylthiocarbamide*, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CS}\cdot\text{NHPh})\cdot\text{N}(\text{CH}_2\text{Ph})\cdot\text{CS}\cdot\text{NHPh}$, colourless needles, m. p. $178-179^\circ$, the *phenylcarbamide*,



colourless, crystalline powder, m. p. 198° , and a *dibenzoyl* derivative, $\text{NHBz}\cdot\text{C}_6\text{H}_4\cdot\text{NBz}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, colourless, crystalline powder, m. p. $179-180^\circ$.

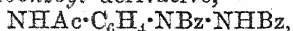
In connexion with the intensely coloured salts of benzaldehyde-*p*-aminophenylhydrazone, the suggestion has been made (*loc. cit.*) that the intensification of the colour may be due to a change in the constitution from the hydrazone to the azo-structure. This explanation becomes untenable in view of the colour of *o*-aminophenyl- β -benzylhydrazine and its hydrochloride, to which azo-structure cannot possibly be attributed. The colour intensity must be due in some way to the presence of the amino-group, because the known phenylbenzylhydrazines and their salts are colourless, but in what way cannot be determined at present; explanations involving quinonoid structure or Wieland's theory of dissociation are shown to be inadequate.

When an alcoholic solution of *o*-aminophenyl- β -benzylhydrazine is boiled with 2*N*-sulphuric or hydrochloric acid, 2-phenylbenziminazole, benzylamine, *o*-phenylenediamine, and ammonia are produced. The formation of these four substances is explained, as in the case of the three similarly obtained from benzaldehyde-*p*-aminophenylhydrazone (*loc. cit.*), by the assumption of the intermediate formation of chloroamines, and an attempt is made to account for the ordinary benzidine and semidine transformations by a similar assumption.

By heating at 120–130° in an atmosphere of hydrogen, *o*-aminophenyl- β -benzylhydrazine is converted into benzaldehyde-*o*-aminophenylhydrazone, benzylamine, and *o*-phenylenediamine. The formation of these is explained by assuming that one molecule of the hydrazine dissociates into $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot$ and $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot$; these are reduced by a second molecule of the hydrazine, which is itself oxidised to the azo-compound, the latter then undergoing rearrangement into the *o*-aminophenylhydrazone. C. S.

Aminohydrazines. IV. *p*-Acetylaminophenylhydrazine and Benzylidene-*m*-aminophenylhydrazine. HARTWIG FRANZEN and BERTHOLD VON FÜRST (*Annalen*, 1916, 412, 35–48). Compare preceding abstract.—It has been shown that certain aminohydrazines form coloured salts and are easily ruptured at the N·N linking by warming with acids, and that these properties are due to the influence of the amino-group. The present investigation has been undertaken to ascertain what will be the effect on these properties of changes in the amino-group.

The crystalline precipitate obtained when diazotised monoacetyl-*p*-phenylenediamine hydrochloride is reduced by stannous chloride according to Riedel's method (D.R.-P., 80843) is not *p*-acetylaminophenylhydrazine hydrochloride, as there stated, but the stannochloride. The hydrochloride is a colourless, indistinctly crystalline substance which is stable by itself and in the presence of cold concentrated hydrochloric acid; the *nitrate* is also a colourless, crystalline powder. The *dibenzoyl* derivative,

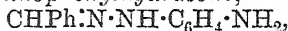


colourless, crystalline powder, has m. p. 155–156°, and the following *p*-acetylaminophenylhydrazones have been prepared: from benzaldehyde, $\text{C}_{15}\text{H}_{15}\text{ON}_3$, pale yellow, crystalline powder, m. p.

195—196° (the alcoholic solution gives with cold dilute hydrochloric or sulphuric acid an almost colourless, flocculent precipitate, whereas benzaldehyde-*p*-aminophenylhydrazine under these conditions gives an intensely violet-red precipitate); from *p*-anisaldehyde, $C_{10}H_{17}O_2N_3$, finely crystalline, red powder, m. p. 170—175°; from pyruvic acid, $C_{11}H_{13}O_5N_3$, deep yellow, crystalline powder, m. p. 192—193°.

When heated with dilute hydrochloric acid, *p*-acetylaminophenylhydrazine hydrochloride remains colourless at first, but then the solution suddenly becomes intensely yellow and nitrogen is evolved; the other products of the decomposition are ammonia, aniline, *p*-phenylenediamine, and acetic acid. It appears, therefore, that the N·N linking is not ruptured until the acetyl-amino-group has been hydrolysed, and that the salts of *p*-aminophenylhydrazine, like those of the ortho-derivative and of benzaldehyde-*p*-aminophenylhydrazine, are intensely coloured.

Benzaldehyde-m-aminophenylhydrazine,



brownish-yellow needles, m. p. 154—155°, is obtained, like the ortho- and para-isomerides (*loc. cit.*), by reducing the corresponding benzaldehyde-*m*-nitrophenylhydrazine with sodium hyposulphite, but the yield is extremely small (14%). The substance is stable, forms a *dibenzoyl* derivative, colourless leaflets, m. p. 210°, and a *phenylthiocarbamide*, $CHPh \cdot N \cdot NH \cdot C_6H_4 \cdot NH \cdot CS \cdot NHPh$, faintly red, crystalline powder, m. p. 138—139°, and yields a *sulphate*, $2C_{13}H_{13}N_3 \cdot H_2SO_4$, colourless needles, m. p. 218°, and *hydrochloride*, colourless leaflets.

From these and the preceding results (*loc. cit.*) the conclusions are drawn: (1) a relation exists between the colour and the stability of the salts of aminophenylhydrazines; coloured salts are very easily ruptured at the N·N linking, whilst colourless salts are not; (2) the loosening effect of the amino-group on the N·N linking is much greater when the amino-group is in the ortho- or para-position than when it is in the meta-position, and is diminished when the amino-group is acetylated.

C. S.

The Phosphorus contained in Animal Proteins after their Demineralisation. L. LINDET (*Bull. Soc. chim.*, 1916, [iv], 19, 395—399. Compare A., 1912, i, 1041).—The protein precipitated from the white of egg by phenol in the presence of 2% acetic acid contains no organic phosphorus. When the vitellin is separated from the yolk of an egg by precipitation with toluene, ether, or 10% saline or 1% phenol, this material, after removal of the fat and washing with 2% acetic acid, contains organic phosphorus to the extent of 3·6—3·7% P_2O_5 on the protein precipitated. The protein of blood contains no organic phosphorus, neither does gelatin or ossein. Of the protein in the fibrin of an ox, the liver of a calf, or the brain of a sheep, the portion which is insoluble in saline solution contains organic phosphorus to the extent of 0·25—1·82% P_2O_5 on the total protein. The flesh of fish contains

no organic phosphorus, either in the portion soluble or insoluble in saline solution. W. G.

The Composition of Neurokeratin. BURT E. NELSON (*J. Amer. Chem. Soc.*, 1916, **38**, 2558—2561).—The neurokeratin was obtained from the total protein residue from several lots of brains of patients having general paresis, senile dementia, and dementia præcox. The minced brain tissues were allowed to remain in 85% alcohol for two months, and then extracted with alcohol, ether, and warm water. The dried protein residue was finely ground and digested at blood heat six times with one hundred times its weight of pepsin-salt-hydrochloric acid mixture and then five times with a 0.1% solution of sodium hydroxide, and finally extracted with alcohol and ether and dried at a gentle heat. The neurokeratin thus obtained was a pale yellow, light powder containing 0.22—0.25% mineral ash. Its elementary composition averaged C, 54.87%; H, 7.28%; N, 13.17%; S, 1.38%; O, 23.07%; ash, 0.23%. Phosphorus was entirely absent. A single partition of the nitrogen content, made by a modification of van Slyke's method, gave: ammonia N, 5.24%; melanin N, 14.51%; arginine N, 2.692%; cystine N, 4.40%; histidine N, 6.279%; lysine N, 11.729%; nitrogen from one or all of pyrroline, oxypyrroline, or tryptophan, 27.95%; nitrogen from one or all of glutamic acid, aspartic acid, tyrosine, leucine, isoleucine, alanine, or glycine, 25.21%. The results of this fractionation indicate that most of the sulphur exists in the form of cystine. W. G.

Formaldehyde as a Prototype of Diastase. Theory of the Action of Diastase. GERTRUD WOKER (*Ber.*, 1916, **49**, 2311—2318).—The author has already shown that formaldehyde can produce the effects of a peroxydase or a catalase, and has explained this by the assumption that the ferments are aldehydic in character and that they form additive compounds with hydrogen peroxide, to which their activities can be traced, thus: $\text{H}\cdot\text{CHO} + \text{H}_2\text{O}_2 = \text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{OH}$. It is now recognised that diastase can behave as a peroxydase or catalase, and the question arises: Can its more important hydrolytic functions be also due to an aldehyde group, or can its action on starch be imitated by formaldehyde? It is conceivable that formaldehyde might form a hydrate which, on decomposition, would offer the elements of water, H and OH, in an active form. Experiments show that solutions of starch and glycogen do, indeed, suffer hydrolysis when left in the presence of relatively large quantities of formaldehyde, although the aldehyde is more pronounced as a prototype of a peroxydase than of diastase. This throws some light on the fact that, although formaldehyde is a powerful poison for enzymes, a 2—5% solution of it actually accelerates the action of diastase. J. C. W.

The Influence of the Hydrion Concentration on the Activity of Malt Diastase. LUDWIG ADLER (*Biochem. Zeitsch.*, 1916, **77**, 146—167).—The optimal hydrion concentration for the

action of this diastase is $p_H=4.9$. Its action is very effective between the limits $p_H=4.6$ and $p_H=5.2$. As the hydron concentration passes these limits in either direction, the activity of the ferment rapidly decreases. Neutral salts are not without action on the diastatic activity, but this influence is small compared with the hydron concentration.

S. B. S.

Studies in Fermentation. II. Autolysis of Starch. W. BIEDERMANN (*Chem. Zentr.*, 1916, ii, 496; from *Fermentforschung*, 1916, 1, 474—504).—The author has previously shown that dilute boiled starch solution can be hydrolysed with comparative rapidity by saliva ash, and that this effect is due to a ferment liberated from the starch under the conditions of experiment. It is now shown that a similar hydrolysis (autolysis) occurs without any addition if the starch solution is made at 70—90°. Reaction occurs considerably more rapidly at 35—45° than at the ordinary temperature, and only the portion of starch which remains in solution suffers autolysis. Solutions which have been actually boiled generally become hydrolysed after a much longer period; extracts prepared by grinding starch with water do so much more rapidly. The diastatic power of the latter is similar to that of a very dilute saliva solution, and transforms starch completely into sugar. Of the salts contained in saliva, the chlorides, particularly calcium chloride, promote diastatic action. The marked action of saliva ash in promoting the decomposition of starch solutions which have been subjected to prolonged boiling suggests that this mixture of salts promotes the new formation of the diastase (amylase) from starch. The action of the ash is much more pronounced than that of the individual chlorides (CaCl_2 , NaCl , KCl) contained in it; artificial mixtures of salts of similar activity have not been prepared up to the present time.

H. W.

Relation of Oxydase Reactions to Changes in Hydrogen Ion Concentration. GUILFORD B. REED (*J. Biol. Chem.*, 1916, 27, 299—302).—In these experiments, extracts of potato or apple containing oxydase are incubated with increasing quantities of acid, the concentration of hydrogen ion in the incubating mixture being estimated by the gas-chain method. The results indicate that the optimal activity of these oxydases is reached when they are in a medium which is very nearly neutral or slightly alkaline. The concentrations of acid which are needed to inhibit oxydase action are found to be much lower than those stated by previous investigators, who have measured the acid added to the oxydase solution, but not the resultant acidity of the medium. As a matter of fact, it is found that a large proportion of the added acid is neutralised by the protein and other amphoteric substances present in the solution.

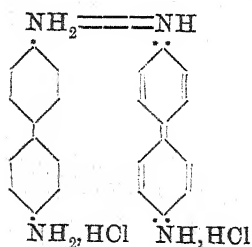
H. W. B.

Theory of the Oxidation of Benzidine in its Significance for Peroxydase Investigations. GERTRUD WOKER (*Ber.*, 1916, 49, 2319—2337).—Kjöllfeldt, a colleague of the author, has ex-

perienced considerable difficulty in the application of benzdine hydrochloride to the determination of peroxydase activities, particularly in the preparation of a reagent of constant and maximum pigment-forming power. He finds that the most active reagent can be obtained by adding enough alkali to the dihydrochloride to neutralise one molecule of the acid, or by adding this quantity of acid to the free base. This salt crystallises in leaflets, is almost insoluble in cold water, and begins to decompose at about 160° , its m. p. being 341° . Other preparations which are more soluble and more stable towards heat have not the same activity. One, of the same acid content (B_2HCl), can be obtained under some conditions, which crystallises in rods, melts without decomposition at $341\text{--}342^{\circ}$, has the solubility 70% at 20° , and gives no blue colour under the influence of a peroxydase.

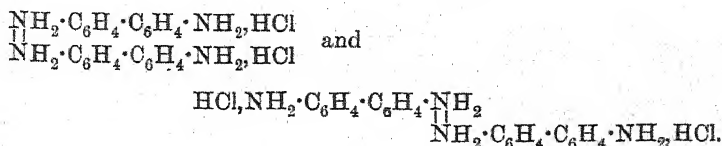
It is furthermore recognised that many of the so-called "activations" and "paralysations" of peroxydases which have been apparently effected by the addition of acids or bases are due to the action of these agents on the test solution, benzdine, and probably not on the ferment at all. The right conditions for the best production of benzdine-blue are realised when the solution contains little or no free hydrochloric acid. The readily soluble hydrochlorides suffer extensive hydrolysis, and their solutions are consequently less active, whilst the insoluble salts are the most active reagents. On keeping, or on washing with water, benzdine dihydrochloride becomes more and more active, owing to the loss of hydrochloric acid.

The oxidation of benzdine is a very complicated question, and the work on the subject is well reviewed. The blue, *meri*-quinonoid oxidation product, which is the one concerned in the



peroxydase reaction, is regarded as a compound of benzenoid benzdine with a quinone-imine molecule and two molecules of hydrogen chloride. Instead of assuming that these molecules are attached by partial valencies, the author prefers the annexed arrangement. This helps to explain the special activity of one benzdine monohydrochloride and the inactivity of another. When the dihydrochloride is deprived of a molecule of hydrogen

chloride, it is assumed that two molecules of the salt participate, giving the *cis*- and *trans*-“dibenzidine” salts,



The *cis*-form is the readily oxidisable one and has the ring systems of the *meri*-quinonoid dye already in it. It may undergo

isomerisation into the inactive *trans*-form under the influence of acids, or acids may break up the double molecule, with the result, in either case, that the salt will be inactive. J. C. W.

Physiological Chemistry.

The "Reduced" and "Regulated" Hydrogen Number of the Blood. OTTO PORGES (*Biochem. Zeitsch.*, 1916, 77, 241—248).—This paper contains a criticism of Hasselbalch's conceptions (A., 1916, i, 519) of the "reduced" (that is, under 40 mm. tension of carbon dioxide) and "regulated" (under the tension of the carbon dioxide of alveolar air) hydrion concentration of the blood. It is based partly on what the author considers a faulty method for the estimation of the tension of carbon dioxide in alveolar air employed by Hasselbalch and his collaborators. The author also objects to Hasselbalch's suggestions as to the employment of the term "acidosis." S. B. S.

The Blood of Participators of an Army March with Accoutrements. II. Residual Nitrogen and its Components, Blood-sugar and Density. JOH. FEIGL (with A. V. KNACK and H. KOOPMANN) (*Biochem. Zeitsch.*, 1916, 76, 297—312. Compare A., 1916, i, 769).—The chief results refer to the residual nitrogen of the blood. In most cases the effect of vigorous exercise is to increase the amount of urea in the blood. S. B. S.

The Total and Residual Reduction by the Blood with Special Reference to the Reducing Components of the Residual Nitrogen; the Estimation of Blood-sugar under Normal and Pathological Conditions. JOH. FEIGL (*Biochem. Zeitsch.*, 1916, 77, 189—231).—A general summary is given, with copious references to the literature, of the work done on estimation of the non-protein nitrogenous constituents of serum and their capacity for reducing reagents employed for estimating sugars. Attempts are made to estimate approximately the deductions to be made in the estimation of sugars due to the presence of such nitrogenous substances in normal and pathological cases ("residual reduction"). Attention is also directed to the influence that can be exerted by the various methods employed for the precipitation of proteins. S. B. S.

Colourless Crystals of Hæmoglobin. D. FRASER HARRIS (*Nature*, 1916, 96, 619; from *Physiol. Abstr.*, 1916, 1, 53).—A note on colourless crystals arising in laked blood and on crystals

originally indistinguishable from hæmoglobin which have become decolorised. Boycott (*ibid.*, 677) suggests that the crystals are serum protein, some of which are tinged with hæmoglobin.

G. B.

Growth. VIII. Influence of a Diet Deficient in Fats, and of the same Diet with Cholesterol added, on the Growth of the White Mouse. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1916, 27, 393—402. Compare A., 1916, i, 690).—A diet composed of potatoes, defatted bran, and white of egg, with the addition of small amounts of chlorophyll and ferric chloride, when fed to young mice leads to initial loss of weight followed by resumption of a retarded growth. Ultimately, however, a sharp decline in weight occurs, which terminates in death about six months after the beginning of the experiment. The addition of cholesterol to the diet prevents the initial loss of weight, but does not prolong the life of the mouse. The author suggests that although growth is possible on the described diet, the tissue produced is unable to be maintained. H. W. B.

Mechanism of Cholesterol Absorption. J. HOWARD MUELLER (*J. Biol. Chem.*, 1916, 27, 463—480. Compare A., 1915, i, 1026).—Experiments in vitro indicate that free cholesterol, in the presence of fatty acids and a suspension of pancreas, undergoes esterification, presumably by the operation of the pancreatic lipase. The action appears to be accelerated by the bile. Ordinary lipases do not saponify cholesterol esters, neither has the reverse action been observed except in the case of the pancreatic lipase already mentioned.

An examination of the intestinal mucosa of the dog reveals the presence of a large amount of esterified cholesterol after feeding. The author suggests that esterification occurs in the lumen of the intestine under the influence of the pancreatic juice, and the esters are absorbed as rapidly as they are formed. H. W. B.

Nutrition and Evolution. II. JACQUES LOEB and J. H. NORTHPROP (*J. Biol. Chem.*, 1916, 27, 309—312. Compare A., 1916, i, 189).—Further experiments with banana flies have shown that successive generations of these insects can be reared on sterile food provided it contains yeast, which appears to be an indispensable food for them. The yeast may be previously heated for an hour at 120°, but cannot be replaced by its alcoholic extract or by butter, milk, nucleic acid, or other material. The necessary substance cannot therefore be identical with the accessory substances indispensable for the growth of pigeons, rats, and other warm-blooded animals.

The results indicate that animals as high in the scale of life as insects could not have existed without the previous existence of yeast. H. W. B.

Calcium Metabolism. I. Deposition of Lime Salts in the Integument of Decapod Crustacea. J. H. PAUL and J. S. SHARPE (*Journ. Physiol.*, 1916, 50, 183—192; from *Physiol. Abstr.*, 1916, 1, 61—62).—After moulting, calcium carbonate is rapidly deposited in the shell of decapod crustaceans. In the edible crab, 80% of the shell is calcium carbonate, but in the lobster, calcium phosphate forms a large bulk of the inorganic matter. In the crab, calcium phosphate is present in the hepatopancreas to the extent of 20% of the bulk of the gland immediately before moulting; after the shell has hardened, this salt is nearly absent from the gland. The lobster, on the other hand, does not store calcium in its hepatopancreas, and the stone crab (*Lithodes maia*) does so only to a slight extent. Before moulting, the hepatopancreas contains 20—50% of oil, which disappears, like the calcium, when the shell hardens. Its iodine value is in inverse order to the quantity of oil and to the quantity of calcium. After moulting, the blood-volume increases tenfold, but its percentage of calcium remains constant. It is present as salts of fatty acids, particularly formic and butyric. G. B.

Mechanism of the Diffusion of Electrolytes through the Membranes of Living Cells. I. The Necessity of a General Salt Effect on the Membrane as a Prerequisite for this Diffusion. JACQUES LOEB (*J. Biol. Chem.*, 1916, 27, 339—352).—Experiments on *Fundulus* eggs are described, the results of which indicate that the diffusion of potassium chloride through the membrane of the egg does not depend only on the osmotic pressure of the potassium chloride solution, but on the production of a certain modification of the membrane, which is termed the "general salt effect." This modification is produced by the action of salts on the external surface or layer of the membrane (presumably on the proteins of the membrane). There is a concentration of the total salts in a solution which accelerates to the greatest extent the diffusion of one of these, for example, potassium chloride through the membrane. When the concentration is increased beyond this optimum, the rate of diffusion is diminished, and eventually the opposite action is observed, namely, the retardation or prevention of the diffusion of the potassium salt. This constitutes the "antagonistic salt action." H. W. B.

Mechanism of the Diffusion of Electrolytes through the Membranes of Living Cells. II. Diffusion of Potassium Chloride out of the Egg of *Fundulus* and the Relative Efficiency of Different Ions for the Salt Effect. JACQUES LOEB (*J. Biol. Chem.*, 1916, 27, 353—362. Compare preceding abstract).—The author finds that eggs previously poisoned with potassium chloride do not recover when put into a solution of any non-electrolyte. When the external surface of the membrane, therefore, is free from salts, it is as efficient a barrier for the diffusion of potassium chloride out of the egg as for diffusion in the opposite direction.

The relative efficiency of different salts for producing the salt effect on the cell-membrane is a function both of anion and cation. The efficiency increases with the valency of the anion approximately according to Hardy's rule, and depends also on the nature of the anion in the following way: chloride<nitrate<bromide<acetate<phosphate, carbonate<sulphate<citrate. With regard to the cation, the salts of sodium, lithium, magnesium, calcium, and ammonium favour the diffusion of potassium chloride through the membrane, whilst barium, strontium, rubidium, and caesium inhibit it.

H. W. B.

Mechanism of the Diffusion of Electrolytes through the Membranes of Living Cells. III. Analogy of the Mechanism of the Diffusion for Acids and Potassium Salts. JACQUES LOEB (*J. Biol. Chem.*, 1916, 27, 363—375. Compare preceding abstracts).—Under certain experimental conditions, the author finds that similar rules hold for the diffusion of acids through the membranes of living eggs of *Fundulus* as for the diffusion of potassium salts. The concentration of neutral salt required for the production of the salt effect is considerably smaller in the case of the diffusion of acid than in that of potassium salt. Very weak acids themselves can supply the general salt effect, owing probably to the fact that acids form stable salts with certain proteins of the membrane, whilst neutral salts form only unstable salts.

When the concentration of neutral salt added to the acid is a little higher than that required for the production of the salt effect, the opposite phenomenon is produced, namely, the diffusion of acid is retarded or arrested (antagonistic salt action).

H. W. B.

The Oxidation of Alcohol by the Liver of Animals which have acquired Tolerance and of those which have not. JULIUS HIRSCH (*Biochem. Zeitsch.*, 1916, 77, 129—145).—In the presence of oxygen and at 37° alcohol is destroyed by the livers of animals which have not acquired tolerance. The capacity for destroying alcohol is either inhibited or annihilated by heating the liver or in the presence of ferment poisons, such as cyanides. The destruction of alcohol is apparently due to a ferment. The pressed juice of the liver dried at the ordinary temperature is also active. The liver paste of animals (rabbits) which have acquired tolerance to alcohol is also active, but not more so than that of normal animals.

S. B. S.

Phosphatides in the Ductless Glands. FREDERIC FENGER (*J. Biol. Chem.*, 1916, 27, 303—307).—Light petroleum extracts relatively larger quantities of phosphatides and fats from the pituitary, suprarenal, pineal, and thymus glands and the corpus luteum than from ordinary muscle tissue. The thyroid gland, on the other hand, contains about the same proportion of these substances as muscle. The author draws the conclusion that phosphatides are

concerned in the operation of most ductless glands, but not in the elaboration of the secretion of the thyroid. H. W. B.

Vital Oxidation of Succinic Acid. The Chemical Kinetics of a Physiological Process. A. WESTERLUND (*Lunds. Univ. Årsskrift*, 1916, 12, [N.F.], reprint, 19 pp.; from *Physiol. Abstr.*, 1916, 1, 133).—The absorption of oxygen by an aqueous solution of succinic acid containing suspended minced horse muscle follows the course of a bimolecular reaction. With excess of the agent, the reaction velocity was computed, by means of the method of least squares, for air mixtures with different percentages of oxygen. The reaction velocity is increased with increasing percentage of oxygen, but only up to a limit, representing the oxygen content of atmospheric air. In a gas mixture with more oxygen the absorption is only accelerated to a very small degree. G. B.

Narcosis. V. RUDOLF HÖBER (*Biochem. Zeitsch.*, 1916, 77, 51—52).—Some remarks on a recent paper by Winterstein (A., 1916, i, 616); the author claims priority to Lillie with regard to certain conceptions as to the action of narcotics on cell permeability. S. B. S.

Narcosis. HANS WINTERSTEIN (*Biochem. Zeitsch.*, 1916, 77, 53—54).—A reply to the above remarks of Höber. S. B. S.

Influence of Parturition on the Composition and Properties of the Milk and Milk Fat of the Cow. C. H. ECKLES and LEROY S. PALMER (*J. Biol. Chem.*, 1916, 27, 313—326).—Colostrum milk obtained after parturition contains relatively large quantities of protein and salts and small quantities of lactose and fat. Colostrum milk fat has a higher melting point and lower saponification and Reichert numbers than ordinary milk fat.

The length of time the cow is dry before parturition is a factor influencing the composition of colostrum milk. The shorter the time the cow is dry, the more closely does the colostrum milk resemble normal milk. When cows are milked up to the time of parturition, both the colostrum milk and milk-fat do not differ greatly from normal milk and milk-fat. The chief difference in these circumstances is an increase in the content of heat-coagulable protein in the milk. H. W. B.

The Connexion between the Metabolism of Phosphates and Carbohydrates in Diabetes. HANS EULER and OLOF SVANBERG (*Biochem. Zeitsch.*, 1916, 76, 326—334).—The effect of the administration to diabetic patients of a preparation made by extraction of dried yeast and separation from the extract of the inorganic phosphates and proteins was investigated. This preparation should contain the co-enzyme. In some cases it caused a diminution of the excretion of sugar in the urine, which was accompanied by a diminution of total phosphates. S. B. S.

Pancreatic Diabetes in the Dog. I. Influence of Alkali and Acid on the Glycosuria and Hyperglycæmia. J. R. MURLIN and B. KRAMER (*J. Biol. Chem.*, 1916, 27, 481—498).—The administration of sodium carbonate has the same inhibiting action on the glycosuria of pancreatic diabetes as is exerted in the case of other glycosuric conditions (compare Pavy and Godden, A., 1912, ii, 68). Hydrochloric acid has the reverse action and increases the glycosuria, whilst sodium and potassium hydrogen carbonates do not produce any marked effect. H. W. B.

Pancreatic Diabetes in the Dog. II. Is the Dextrose retained when Sodium Carbonate is administered to Depancreatized Dogs deposited as Glycogen? B. KRAMER, J. MARKER, and J. R. MURLIN (*J. Biol. Chem.*, 1916, 27, 499—515. Compare A., 1916, i, 348, and preceding abstract).—A full account of work previously published. H. W. B.

Pancreatic Diabetes in the Dog. III. Influence of Alkali on the Respiratory Metabolism after Total and Partial Pancreatectomy. J. R. MURLIN and B. KRAMER, with J. A. RICHE (*J. Biol. Chem.*, 1916, 27, 517—538. Compare preceding abstracts).—The administration of sodium carbonate to partially depancreatized dogs is followed by an increase in the respiratory metabolism, which is not observed in the case of fully depancreatized animals. H. W. B.

Maize Diet and its Connexion with Pellagra. P. SUÁREZ (*Biochem. Zeitsch.*, 1916, 77, 17—26).—A method is described for the extraction of the fluorescing substance which is contained in maize. It is shown that this acts photodynamically on red blood corpuscles and on *Paramoecium coli*, and also on rabbits at the point of injection. On the other hand, the administration of "zeochin," as the fluorescing substance is called, when added to their diet, produces no photodynamic effect on mice. When, however, mice or pigeons have been fed on a diet composed exclusively of maize, they develop an illness similar to beriberi, the symptoms of which rapidly disappear after administration of yeast. The assumption is made by the author that pellagra is due to a deficiency of some accessory food-stuff in the diet, and that on the same diet, in the condition produced by the deficiency, the "zeochin" exerts a photodynamic effect. S. B. S.

The Sensitising Action of the Natural Porphyrins. WALTHER HAUSMANN (*Biochem. Zeitsch.*, 1916, 77, 268—272).—A crude porphyrin obtained from the urine of a patient with lead-poisoning was photodynamically active when tested with red blood corpuscles and paramoecia. The porphyrin of the worm *Eisenia foetida*, which in vivo acts as a protection against light, can act as a light sensitiser in vitro. Hence one and the same pigment can exist in a sensitising and non-sensitising form. Facts of this description show the possibility of porphyrinuria with and without light sensibility. S. B. S.

A New Group of Antagonising Atoms. I. T. P. FEENSTRA (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, 19, 99—104).—If a Ringer-Locke solution from which the potassium salt has been omitted is perfused through a frog's heart, the latter, as is well known, ceases to beat after a certain time in diastole. It has been found by the author that the addition of uranium nitrate in certain quantity to the potassium-free Ringer fluid can cause the heart to beat again normally. Too large an excess of uranium salt will, however, cause heart action to cease again, but this action can be antagonised by the addition of more calcium salt. In a Ringer solution, the ratio of $\text{UO}_2(\text{NO}_3)_2 : \text{CaCl}_2$ appears to be about 1:24. S. B. S.

Fate of Alkali-Blue in the Organism. SHIGENOBU KURIYAMA (*J. Biol. Chem.*, 1916, 27, 377—391).—Alkali-blue injected intravenously into rats, rabbits, or dogs appears rapidly in the lymph in both leuco and free forms. The lymph flow is not markedly affected by the injection of the dye.

When administered parenterally, alkali-blue is eliminated chiefly in the bile. It appears to act as a cholagogue. It is not eliminated by the kidneys (except in traces), nor, after intravenous injection, by the alimentary tract. H. W. B.

Physiological and Pharmacological Studies on Coal-tar Colours. I. Fat-soluble Dyes. WILLIAM SALANT and ROBERT BENGIS (*J. Biol. Chem.*, 1916, 27, 403—427).—Fat-soluble dyes, when given to rats, cats, or rabbits with the food or injected subcutaneously or intravenously, are eliminated in the urine and in the bile. In two particular cases it was found that the dyes were eliminated in the form of conjugated glycuronates. *Benzene-azoresorcinol glycuronate*, $\text{C}_{18}\text{H}_{20}\text{O}_9\text{N}_2$, crystallises in long, yellow prisms, m. p. 189—190° (decomp.). *Benzeneazophenol glycuronate*, $\text{C}_{18}\text{H}_{20}\text{O}_8\text{N}_2$, crystallises from dilute alcohol in yellow, rectangular plates or, sometimes, acicular prisms, m. p. 164—165° (decomp.). On hydrolysis, the corresponding dyes are obtained. It is probable that similar compounds were formed in the cases of the other dyes examined, although they were not isolated from the urine.

Histological examination showed that most of the dyes were deposited in the adipose tissue; staining of the nervous tissue, the kidney, and muscle was also observed in some experiments. The toxicity of the dyes was not pronounced even when large doses were administered. H. W. B.

The Pharmacology of Saponins. A. W. VAN DER HAAR. (*Biochem. Zeitsch.*, 1916, 76, 350—358).—Some experiments showing differences in different preparations of saponin as regards toxicity to fish and frogs, and also as to hæmolytic action.

S. B. S.

The Action of Cobra Poison on Lecithin. R. KUDICKE and H. SACHS (*Biochem. Zeitsch.*, 1916, 76, 359—376).—Calcium

chloride, in not too high concentrations, stimulates the hæmolysis by cobra poison of blood corpuscles which are sensitive to its influence. It can also stimulate the combined action of cobra poison and lecithin on other corpuscles, and appears to assist the fermentative action of cobra poison, which produces the scission of fatty acids from lecithin. It is not possible to state how far the action of calcium chloride is intracellular or extracellular.

The hæmolysis of non-sensitive corpuscles by cobra poison in isotonic solutions of sucrose is inhibited to a greater extent by calcium than by sodium chloride. The hæmolysis by joint action of cobra poison and lecithin in solutions of sucrose is inhibited by calcium chloride, although the hæmolysis in presence of equal quantities both in sucrose and sodium chloride solutions is stronger than in pure sodium chloride solutions. In the presence of a small amount of lecithin, calcium chloride has an inhibitory action. The action of the lecithide alone is diminished by heating, especially in more dilute solutions (in the latter case even at 37°). This diminution of action is increased by the addition of cobra poison, especially in presence of calcium salts.

The results generally confirm the conceptions of Delezenne and Ledebt, namely, that cobra poison exerts a fermentative action on lecithin, yielding a strongly hæmolytic lecithide as intermediary product; the latter undergoes, under the influence of the cobra poison, a further fermentative change to yield an end-product without hæmolytic action. Both phases of the change in lecithin are promoted by the presence of calcium salts.

S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

General Conceptions of Intoxication. III. The Stimulative Action of Lecithin on Ferment Formation. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, 77, 124—128. Compare A., 1916, i, 778).—The scission of urea by bacteria is not influenced by cholesterol, but is accelerated by "Agfa" lecithin; the latter substance does not, however, exert a similar influence on the urease action of soja bean. These results indicate that the lecithin stimulates the production of the ferment, but not the action of the ferment itself.

S. B. S.

The Activators of Fermentation. HANS EULER and HARALD HAMMARSTEN (*Biochem. Zeitsch.*, 1916, 76, 314—320).—It has been shown by Euler and Cassel (A., 1913, i, 1025) that the addition of ammonium formate and other substances increases the fermentation of yeast. It is now found that the formate does not also increase the amount of yeast formed. It is also found that the

addition of phosphates, which increases the rate of fermentation in acid (but not in alkaline solutions), does not cause a parallel increase in the growth of the yeast.

S. B. S.

Formation of Albumin from Different Sources of Carbon.

TH. BOKORNY (*Chem. Zentr.*, 1916, ii, 153; from *Münch. med. Woch.*, 1916, 63, 791—792).—The question has been particularly studied with yeast, in the large-scale production of which the carbon nutriment is the most difficult problem. Although carbamide can serve as a source of nitrogen, its carbon is not assimilated by yeast. According to the investigations of Naegeli and others, organic acids (citric, acetic, tartaric), as well as glycerol, asparagine, peptone, mannitol, and other carbohydrates, can be used as sources of carbon for yeast, and the nature of the latter determines the utility of the different sources. Pentoses are unfermentable, but, in suitable circumstances, can serve as sources of carbon. Dextrins are scarcely fermented by yeast cultures, but readily by crude yeast. Alcohol is utilised as a source of carbon by many moulds and bacteria. The growth of many yeasts is more vigorous in alcohol than in sugar. Brewer's yeast requires the presence of sugar during cultivation because the fermentation is a protection against bacteria. The development of other moulds is checked by the rapid formation of alcohol. Attempts to replace a portion of the sugar by methyl alcohol were unsuccessful, but good results were obtained with glycerol.

H. W.

Influence of Alcohol Concentration and Temperature on the Biochemical Synthesis of α -Methylgalactoside.

AUBRY (*J. Pharm. Chim.*, 1916, [vii], 14, 289—294. Compare A., 1914, i, 253, 498; 1916, i, 711).—Further evidence is produced in support of the view that the enzymes present in bottom yeast, causing the synthesis or hydrolysis of α -glucosides and α -galactosides respectively, are two distinct ferments. α -Galactosidase is much more resistant to the injurious influence of methyl alcohol than α -glucosidase. At the ordinary temperature the optimum alcohol concentration is between 20 and 30 grams per 100 c.c., at which concentration about 65% of the galactose present is converted into galactoside. When the alcohol concentration reaches 40 grams per 100 c.c. the enzyme is rapidly destroyed. Rise in temperature reduces the resistance of the enzyme to the influence of methyl alcohol, the maximum temperature advisable being 20—22°.

W. G.

Poisoning of Enzymes in the Living Cell.

HANS EULER and BETH EULER (*Chem. Zentr.*, 1916, ii, 405—406; from *Fermentforschung*, 1916, 1, 465—470).—The authors have endeavoured to determine to what extent yeast suffers permanent damage after its fermentative power has been lessened by poison. Resorcinol has been used in the latter capacity, since that part of it which has not penetrated into the cell can be readily removed. In 0.5% solution the fermentative power of yeast is not completely destroyed

in twenty-four hours, but this effect is produced by a 2% solution; all the cells are not killed, however, since fermentation sets in to some extent when the yeast is transferred to a non-poisonous sugar solution. 0.5% Resorcinol, unlike a similar amount of toluene, does not promote the fermentation of sodium pyruvate by yeast, but it must not be assumed that resorcinol at this concentration alters to any extent the permeability of the cell membrane for the fermentable substance. The degree of poisoning probably depends on the amount of poison absorbed. The activity of yeast is increased by minute quantities of resorcinol, a maximum action being observed at a concentration of about 0.0015%. Since from solutions of resorcinol of concentration 0.5% not more than 5% of the poison disappears, it is calculated that the maximum lies at the highest at 1—2 gm.-mol. of resorcinol to 1 gm.-mol. of albumin. H. W.

The Metabolism of *Aspergillus niger*. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, 19, 215—218).—It is shown that the amounts of carbon, hydrogen, nitrogen, phosphorus, and inorganic elements present in the fungus diminish as the organism grows older. All elements needed for the metabolism of *Aspergillus niger* are accumulated in the young fungus material, and when this gets older they are excreted. At a certain stage, therefore, absorption of any element from the nutrient media is no longer essential for normal metabolism. S. B. S.

Catalytic Role of Potassium Nitrate in the Alcoholic Fermentation produced by *Aspergillus niger*. MARIN MOLLIARD (*Compt. rend.*, 1916, 163, 570—572).—In the presence of potassium nitrate to the extent of 2 parts per 1000 of culture liquid the alcoholic fermentation produced by *Aspergillus niger* is much more prolonged and about 3.3 times more considerable than in the presence of the same amount of ammonium chloride. This increase is not due to a greater development of mycelium, nor is there any denitrification during the fermentation. The optimum amount of potassium nitrate for this process is 4 parts per 1000. W. G.

Photographic Detection of Emanations in Biological Processes. F. SCHEMINZKÝ (*Biochem. Zeit.*, 1916, 77, 14—16).—A photographic plate is placed in a box in the bottom of which a figure is cut out (cross, etc.), and this rests on a black photographic dish, in which the various biochemical processes take place. The whole is enclosed in a dark box covered with a lid. If fermentation (yeast), germination (phaseolus), or putrefaction is allowed to take place in the black dish, the emanations pass through the figure in the box holding the plate, which on development exhibits this figure. Photographic illustrations accompany the paper. S. B. S.

Origin and Distribution of Carbamide in Nature. Application of New Methods of Estimation of Carbamide, based on the use of Xanthidrol. R. FOSSE (*Ann. Chim.*, 1916, [ix], 6, 13—95, 155—215).—A more detailed account of work

already published (compare A., 1905, i, 541, 917; 1906, i, 687; 1912, i, 519, 541, 668, ii, 1203; 1914, i, 790, 859, ii, 154, 506, 593, 756, 757).
W. G.

Some Photochemical Experiments with Pure Chlorophyll and their Bearing on Theories of Carbon Assimilation.

INGVAR JÖRGENSEN and FRANKLIN KIDD (*Proc. Roy. Soc.*, 1916, [B], 89, 342—361).—Experiments were carried out with a sol of pure chlorophyll (a mixture of chlorophylls A and B) in water. On exposure to light in the presence of nitrogen, no change takes place; in the presence of carbon dioxide, chlorophyll is converted into pheophytin without any further change; no formaldehyde is produced. In the presence of oxygen, the first change is the yellowing, followed by the bleaching of the pigment. During the first stages of the change the formaldehyde production is slow, but after bleaching is complete the amount formed rapidly reaches a maximum and then diminishes. The acidity of the system increases continuously; apparently the formaldehyde undergoes oxidation in the presence of light and oxygen. The general results do not support the various hypotheses which have been suggested to explain the mechanism of carbon assimilation by green plants.

S. B. S.

Selective Permeability; the Absorption of Phenol and other Solutions by the Seeds of *Hordeum vulgare*.

ADRIAN J. BROWN and FRANK TINKER (*Proc. Roy. Soc.*, 1916, [B], 89, 373—379).—Estimations were made of the amounts of phenol, aniline, and acetic acid which enter barley seeds from solutions of varying concentration. From the results, together with those obtained from earlier investigations, the conclusion is drawn that the most strongly absorbed substances are those which give solutions having very low surface tensions. The fact that solutes giving solutions of high surface tension do not, as a rule, permeate the membrane, suggests that the selective action of the latter is due to selective adsorption.

S. B. S.

Presence of Nitrites and Ammonia in Diseased Plants. Its Significance with Regard to Crop Rotation and Soil Depletion.

P. A. BONCQUET (*J. Amer. Chem. Soc.*, 1916, 38, 2572—2576).—Nitrites have not been detected in any plant tissue which was normal in the strictest sense of the word. In the case of (1) sugar beets affected with curly leaf and containing *Bacillus morulans*, (2) tobacco leaves affected with the "Mosaic Disease," and (3) potatoes infected with *Streptococcus solani*, n.sp., the juices of the leaves were always found to contain nitrites, and in some cases ammonia. The affected potato tubers only showed traces of nitrites, due to the fact that normal tubers only contain traces of nitrates. Several other plants, such as lucerne, bean, and *Malva rotundifolia*, showing abnormalities in leaf or stem structure, gave a decided nitrite reaction. It was shown that the juices obtained aseptically from all the above abnormal plants gave

abundant reduction in vitro of nitrates when inoculated in nitrite-free peptone tubes, together with a considerable bacterial growth.

In the case of a field which had been planted with potatoes for more than fifteen years, nearly every vine showed signs of nitrogen starvation due to internal bacterial reduction, although the soil was abundantly supplied with nitrates. Lack of crop rotation in this case, and also in beet fields, increases the virulence of nitrate-reducing bacteria as invaders of plant tissues, the yield of crop being reduced in some cases to such a point as to be attributed to soil depletion. W. G.

Physiological Balance of Nutrient Solutions for Plants in Sand Cultures. ARTHUR G. MCCALL (*Soil Sci.*, 1916, 2, 207—253).—The results of sand-culture experiments with wheat manured with potassium dihydrogen phosphate, calcium nitrate, and magnesium sulphate showed that the greatest yields were obtained when the total concentration of the nutrient solutions was between 1 and 2 atmospheres of osmotic pressure.

Further experiments are described in which the effect of thirty-six different proportions of the same salts were determined, the total concentrations (1.75 atmosphere) and other conditions being the same. The results are discussed in detail and are compared with those obtained in water-cultures (J. W. Shine, *Physiol. Research*, 1915, [v], 1, 327). The results obtained in sand-cultures correspond more nearly with those obtained in Shive's sub-optimal solution than those obtained with the optimal solution, and there was a marked difference between the solutions producing the best growth in sand- and in water-cultures.

The average ratios of calcium nitrate to magnesium sulphate in the nine best and the nine worst cultures were respectively 2.4:1 and 1:2.9. It is possible, however, that the better results were due to the increased amounts of nitrate, and not to the relation of calcium to magnesium. N. H. J. M.

The Connexion between Acid Taste and Hydrogen-Ion Concentration. THEODOR PAUL (*Ber.*, 1916, 49, 2124—2137).—It frequently happens that a wine which is judged to be more acid to the taste than another, actually reveals less acid when titrated. If, however, the hydrogen-ion concentration is determined by, for example, studying the inversion of sucrose, then it is found that the more sour-tasting wine has the higher H-ion content. The addition of a salt with the same ion (potassium tartrate) lowers the H-ion concentration, and a wine so treated becomes less sour-tasting in proportion to the amount of tartrate added.

The details of the experiments, in which a number of professional wine-tasters participated, are fully recorded, and the number of milligram-H-ions per litre is suggested as a criterion ("acid-degree") for a wine. J. C. W.

Soluble Non-protein Nitrogen of the Soil. R. S. POTTER and R. S. SNYDER (*Chem. Zentr.*, 1916, ii, 237; from *J. Agric. Research*, 6, 61—64).—The authors have investigated the extent

of the decomposition of organic substances in the soil by estimating the amount of soluble nitrogenous material which remains after precipitating the proteins by a suitable reagent. With this object, they have determined the nitrogen content of alkali extracts of soil with and without addition of nitrogenous substances (glutamic acid, hippuric acid, guanine, guanidine, carbamide, hypoxanthine, scatole, etc.), and, in addition, the nitrogen content of the filtrates after precipitation of the proteins from the alkali extracts by means of trichloroacetic acid. They are led to the conclusion that the alkali extracts do not contain any definite class of compounds, and that the filtrates, after removal of proteins, appear to contain the simpler nitrogenous non-protein substances. Investigation of the filtrates should therefore be a guide to the degree of decomposition of organic compounds in the soil. H. W.

Organic Phosphorus of the Soil. R. S. POTTER and T. H. BENTON (*Soil Sci.*, 1916, 2, 291—298).—Estimations of total and organic phosphorus in alkali extracts of several soils. The method employed was a combination of those of Forbes (*Ohio Agric. Exp. Stat. Bull.*, 215) and Emmet and Grindley (*J. Amer. Chem. Soc.*, 1906, 28, 25), both modified. The results showed that a considerable portion of the phosphorus extracted from soils is in organic forms, and that the proportion of organic to inorganic phosphorus was lowest in the soils of plots which received the more inert organic matter, such as peat and oat straw. N. H. J. M.

The Destruction of Underground Building Work by Moorland Sulphur. HANS KÜHL (*Zeitsch. angew. Chem.*, 1916, 29, i, 335—336. Compare Thörner, A., 1916, i, 590).—Not only is the so-called 'reactive sulphur' destructive towards underground building work, but also that which occurs as sulphates of calcium and magnesium so far as cement work is concerned, for apart from the action of free sulphuric acid derived from the 'reactive sulphur,' the above soluble sulphates by penetrating into the cement give rise to the formation of a voluminous, almost insoluble double compound of calcium aluminate and calcium sulphate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4$, a reaction overlooked by Thörner (*loc. cit.*). Consequently, soluble sulphates must have a similar corrosive action on the cement to that of free sulphuric acid. G. F. M.

Nature of the Sulphur of Peat Soils. WILH. THÖRNER (*Zeitsch. angew. Chem.*, 1916, 29, i, 363—364. Compare A., 1916, i, 590).—A reply to Kühn (preceding abstract). Calcium and magnesium sulphates occur in most peat soils only in small amounts; exceptions occur in soils near the sea owing, probably, to the presence of considerable amounts of these salts in the soil water. This water may, undoubtedly cause injury to the foundations of buildings.

Under ordinary conditions the sulphates present in peat are not injurious to vegetation or to buildings. N. H. J. M.

Organic Chemistry

Production of the Lower Chlorides of Methane from Natural Gas. CLAYTON W. BEDFORD (*J. Ind. Eng. Chem.*, 1910, 8, 1090—1094).—By subjecting a mixture of chlorine and natural gas, in a chamber containing blocks of ice, to the action of light from the white-flame arc, a heavy liquid was obtained beneath the water produced by the melted ice; this liquid consisted of methylene chloride, 35%; chloroform, 33%; carbon tetrachloride, 5%; and ethane chloro-derivatives, 20%. A portion of the product, amounting to about 14% of the total, remained soluble in the water, and consisted of methylene chloride, 61%; chloroform, 28%; carbon tetrachloride, 1.5%; and ethane chloro-derivatives, 6%. Two hundred and fifty cubic feet of the natural gas yielded several gallons of the mixed chlorides. W. P. S.

Preparation of Carbon Tetrachloride. THE DOW CHEMICAL Co. (U.S. Pat., 1204608; from *J. Soc. Chem. Ind.*, 1916, 35, 1271—1272).—Carbon tetrachloride is prepared by the action of carbon disulphide on sulphur dichloride in such quantity that the latter is reduced practically to the monochloride; the temperature is then raised and more carbon disulphide added until the monochloride is reduced to sulphur. The process may be modified by carrying on the first stage until the residue consists of a hot solution of sulphur in sulphur monochloride, adding more sulphur dichloride, and continuing the addition of carbon disulphide until the same point is reached again, and finally raising the temperature and adding carbon disulphide until the residue, which is kept liquid, consists mainly of sulphur. The carbon tetrachloride evolved in the reactions is condensed. H. W.

Preparation of β -Chloroisopentane. BADISCHE ANILIN- & SODA-FABRIK (U.S. Pat., 1202282; from *J. Soc. Chem. Ind.*, 1916, 35, 1235).—A mixture of petrol hydrocarbons, chiefly pentane and isopentane, is chlorinated; hydrogen chloride is eliminated from the separated monochloropentanes by a suitable reagent, and the olefines obtained are treated with hydrogen chloride. The β -chloroisopentane thus formed is separated, the residue treated with an isomerising agent, and more β -chloroisopentane produced by the action of hydrogen chloride. The processes of separation, isomerisation, and treatment with hydrogen chloride may be repeated until practically the whole of the olefine is converted into β -chloroisopentane. H. W.

Derivatives of Trihalogeno-*tert.*-butyl Alcohols. I. The Acetic Ester of Tribromo-*tert.*-butyl Alcohol or Brometone Acetic Ester. T. B. ALDRICH and C. P. BECKWITH (*J. Amer. Chem. Soc.*, 1916, 38, 2740—2746. Compare A., 1916, i, 115).— β -Tri-

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bromomethylpropan- β -ol, $\text{CBr}_3 \cdot \text{CMe}_2 \cdot \text{OH}$, is converted into the corresponding *acetate*, $\text{CBr}_3 \cdot \text{CMe}_2 \cdot \text{OAc}$, a white solid, m. p. 43–44°, by heating it either with a mixture of acetic anhydride and sodium acetate for two hours, or with acetyl chloride or bromide in acetic acid solution. In its properties, the acetate resembles the corresponding chloro-compound (*loc. cit.*). It is somewhat similar to chloretone in its pharmacological action, but its action is weaker and less rapid than that of chloretone.

W. G.

The Constituents of Wool Fat. F. RÖHMANN (*Biochem. Zeitsch.*, 1916, 77, 298–328).—A detailed account is given of attempts to separate the constituents of wool fat. As a result of the experiments, the author draws the conclusion that wool fat consists of a mixture of the esters of cholesterol and of alcohols of the fatty series, including ceryl alcohol and alcohols with a smaller number of carbon atoms. He was unable to confirm the presence of carnaubyl alcohol or of *ischolesterol*. The fatty acids are apparently cerotic, palmitic, and stearic acids in the more solid constituents of the fat. The more liquid constituents of the fat contain, in addition to free cholesterol, a mixture of alcohols of an oily nature, and the fatty acids are probably stearic and palmitic acids, and an optically active acid (hydroxystearic acid?), together with resin acids. From the more solid constituents of the fat there was found, in addition, mixed with the fatty acids, a substance, m. p. 103°, which may be the anhydride of lanoceric acid. Carnaubic acid, which has been described as a constituent of wool fat, is regarded by the author as a mixture of cerotic acid with acids containing a smaller number of carbon atoms. S. B. S.

Esters of Oleic Acid and their Hydrogenated Products. CARLETON ELLIS and LOUIS RABINOVITZ (*J. Ind. Eng. Chem.*, 1916, 8, 1105–1108).—The methyl, ethyl, propyl, *isobutyl*, amyl, benzyl, and glyceryl esters of oleic acid were prepared; they were oily liquids at the ordinary temperature. These esters, when hydrogenated in the presence of reduced nickel, yielded products which were practically saturated. The nature of the alcohol did not seem to affect to any great extent the rate or degree of hydrogenation. A substance, prepared by heating oleic acid with aniline, hydrogenated readily, and yielded a hard, brittle mass, m. p. 76°.

W. P. S.

Solubility of Alkali Oxalates in the Presence of some Alkali Salts. A. COLANI (*Bull. Soc. chim.*, 1916, [iv], 19, 405–407).—The author has determined the solubility of potassium oxalate in the presence of potassium chloride, potassium sulphate, or potassium nitrate, and the solubilities of sodium and ammonium oxalates in the presence of the corresponding sodium and ammonium salts at 15° and 50°, the solutions being saturated with respect to the two solid phases. The results are tabulated.

W. G.

Variations of the Rotatory Power of Galactose and Dextrose in Propyl Alcohol at Different Concentrations. D. FOULKES (*J. Pharm. Chim.*, 1916, [vii], 14, 364—366).—The rotatory power of galactose diminishes, and of dextrose increases, as the solution becomes richer in propyl alcohol. W. G.

The Optical Rotation and Cryoscopic Behaviour of Sugars Dissolved in (a) Formamide, (b) Water. II. JOHN EDWIN MACKENZIE and SUDHAMOY GHOSH (*Proc. Roy. Soc. Edin.*, 1916, 36, iii, 204—215).—The authors have now extended their work (compare A., 1915, ii, 301) to a study of β -*D*-glucose, β -*D*-galactose, and maltose. Molecular-weight determinations gave no indication of association of the sugar molecule. The mutarotation in formamide solution has now been measured, starting from both the α - and β -forms of *D*-glucose, *D*-galactose, and lactose. As in the case of the aqueous solutions of these sugars, the constant rotation shown where there is equilibrium between the two modifications is found to be the same whether the starting point be the α - or the β -modification. The authors suggest that the mechanism of mutarotation may be due to the formation of a compound, such as is known in the case of β -glucose and pyridine, and subsequent splitting off of the pyridine or formamide molecule, with formation of α - and β -forms. W. G.

Evidence Indicating the Existence of a New Variety of Fructose. A Reactive Form of Methylfructoside. JAMES COLQUHOUN IRVINE and GEORGE ROBERTSON (*T.*, 1916, 109, 1305—1314).—It has been shown that glucose can exist not only as the ordinary α - and β -isomerides of a butylene oxide type, but also as highly reactive " γ -glucose," which is probably analogous to ethylene oxide (A., 1915, i, 381). The idea naturally occurs that other hexoses may also conform to this " γ -glucose" type, and a review of the literature shows that a large number of facts are known which are not explained by butylene oxide formulations. Notably, the extreme ease with which sucrose is hydrolysed would suggest that either the glucose or fructose fragment in it conforms to γ -glucose. It has been proved, however, that the glucose fragment is present identically as it is in α -methylglucoside (*T.*, 1905, 87, 1022), from which it naturally follows that the fructose may have the γ -glucose structure, and, consequently, that the prevailing formula for sucrose needs to be corrected (see Haworth and Law, next page).

An examination of the methylfructosides has now revealed the existence of a type corresponding with γ -methylglucoside, which therefore probably contains the ethylene-oxide ring. This reacts so readily with acetone to form *methylfructosidemonoacetone*, $C_{10}H_{18}O_6$, a vitreous mass, b. p. 142—145°/0.05 mm., that even the trace of acetone commonly present in methyl alcohol is involved in this condensation during the production of the methylfructosides. Much that was obscure in previous work on the changes in rotation which result when fructose is condensed with

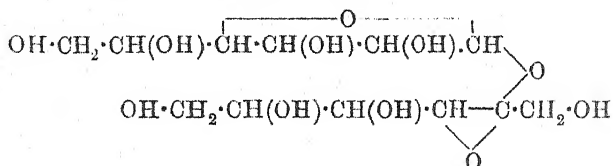
methyl alcohol can therefore be explained. At least four methyl-fructosides are formed, the stereoisomeric α - and β -forms of the butylene oxide type and the α - and β -forms of the ethylene oxide type, and the condensation of these with the traces of acetone still further complicates matters.

J. C. W.

The Sublimation of Sugars. SUDHAMOY GHOSH (*Proc. Roy. Soc. Edin.*, 1916, **36**, iii, 216—218).—Rhamnose or its hydrate, when heated at 105° under a pressure of 1—2 mm., sublimes slowly, and the sublimate obtained has all the physical properties of anhydrous rhamnose, and gives the same phenylosazone. At from 1—2 mm. pressure and about 100°, lævulose also sublimes, but much less rapidly than rhamnose.

W. G.

Constitution of the Disaccharides. I. Structure of Sucrose. WALTER NORMAN HAWORTH and JAMES LAW (*T.*, 1916, **109**, 1314—1325).—When octamethylsucrose is hydrolysed by means of hydrochloric acid, the rotation only changes from $[\alpha]_D + 66.7^\circ$ to $+57^\circ$, whereas a mixture of the known crystalline tetramethylglucose and tetramethylfructose would be lævorotatory, like invert-sugar. Purdie and Paul, however, have shown that an oily, dextrorotatory tetramethylfructose can be obtained (*T.*, 1907, **91**, 294), and reasons are now given for assuming that this belongs to the type of γ -fructose, that is, it contains in all probability an ethylene-oxide structure. It follows, therefore, since the glucose fragment is of the normal type (crystalline tetramethylglucose can be isolated), that the abnormal rotation must be due to the new γ -fructose form, that is, that when octamethylsucrose is hydrolysed, it yields the α - and β -forms of butylene-oxidic tetramethylglucose and the α - and β -forms of ethylene-oxidic tetramethylfructose. Consequently, the original sucrose contains the ethylene-oxidic fructose, and should be formulated thus:



The hydrolysis of sucrose can therefore no longer be regarded as a very simple process, for it may involve the production of the α - and β -forms of butylene-oxidic glucose and ethylene-oxidic fructose, and then the change of these into the more stable α - and β -butylene-oxidic fructoses.

J. C. W.

The Consistency of Pectin Gels. JAS. B. MCNAIR (*J. Physical Chem.*, 1916, **20**, 633—639).—The active substances concerned in the preparation of fruit jellies are supposed to be pectin, sucrose, and acid. The behaviour of solutions containing the two first-mentioned substances and citric acid has been examined, and it is found that jellies may be obtained when the concentrations are

suitably chosen. Jellies are also formed in the absence of the acid, but the pectin concentration required is considerably greater.

H. M. D.

Influence of Acid Radicles Containing Different Secondary Alkyls on the Narcotic Action of Urethane. ISAO ODAIRA (*Mem. Coll. Sci. Kyoto*, 1916, 1, 319—340).—The author has synthesised a number of derivatives of urethane, and examined their physiological activities.

α -Ethylbutyrylurethane ("detonal"), $\text{CH}_3\text{Et}_2\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, from urethane and the acyl chloride, forms colourless needles, m. p. 88° ; α -ethylvalerylurethane ("epronal"), $\text{CH}_3\text{EtPr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, has m. p. 72° ; α -propylvalerylurethane ("dipronal") has m. p. 88 — 89° ; α -propylhexoylurethane ("probnal") has m. p. 69 — 70° ; α -butylhexoylurethane ("dibnal") has m. p. 44° . The solubilities of these compounds in cold water decreases with increasing molecular weight. n-Heptylurethane crystallises in thin plates, m. p. 67° ; isoamylurethane, $\text{CH}_3\text{Et}_2\text{NH}\cdot\text{CO}_2\text{Et}$, is a colourless, fragrant oil, b. p. 155° (460 mm.); α -bromo- α -ethylvalerylcaramide, $\text{CBrEtPr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, forms an opaque liquid at 97° , which is clear at 105° .

Physiological experiments are described in which these compounds are compared with urethane and other common narcotics. It appears that the secondary alkyl group has a greater modifying influence than the primary alkyl, and that the narcotic activity is enhanced by lengthening the chain in the substituent. The acyl group as such has not much influence on the narcotic power, but diminishes the toxicity of the urethanes.

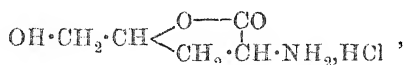
It has been suggested that the narcotic effect of a substance depends on the coefficient of its distribution between oil and water. The partition coefficients of some of these drugs have been determined for olive oil and water, and it is found that, whilst they do not harmonise with the duration of the narcosis, the promptitude with which the substance acts is the more the higher its coefficient.

The paper is illustrated by a blood-pressure curve for a rabbit under the influence of "epronal," which shows that the vagus and respiratory centre are uninfluenced.

J. C. W.

The Synthesis of Amino-Acids. α -Amino- γ -dihydroxyvaleric Acid; γ -Hydroxyproline; α -Diamino- γ -hydroxyvaleric Acid. EINAR HAMMARSTEN (*Compt. rend. Lab. Carlsberg*, 1916, 11, 223—262).—Allylhippuric acid (compare Sørensen, this vol., i, 89) gives an ethyl ester, m. p. 54.5° , which when brominated in chloroform solution yields ethyl γ -dibromo- α -benzoylaminovaleric acid, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}(\text{NHBz})\cdot\text{CO}_2\text{Et}$, m. p. 96.5 — 97.5° . The corresponding acid was obtained in the solid state, m. p. 203 — 204° (compare Sørensen, A., 1908, i, 981), as was δ -bromo- α -benzoylamino- γ -valerolactone, m. p. 162.5 — 163° , when the dibromo-acid was boiled with water or acted on in cold alcoholic solution with aqueous barium hydroxide. This lactone, on further

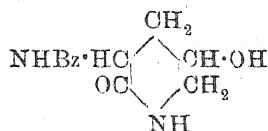
treatment with barium hydroxide, yielded α -benzoylamino- δ -hydroxyvalerolactone, m. p. 167—168°, which when heated on a water-bath with concentrated hydrochloric acid gave α -amino- δ -hydroxy- γ -valerolactone hydrochloride,



m. p. 189—193°. From this hydrochloride, α -amino- $\gamma\delta$ -dihydroxyvaleric acid was obtained in the form of its copper salt (compare Fischer and Krämer, A., 1908, i, 858).

The filtrate from the preparation of δ -bromo- α -benzoylamino- γ -valerolactone gave 4-benzoyloxyproline, m. p. 158—161°, which was first isolated in the form of its copper salt. From this benzoylated proline, the two copper salts of 4-hydroxyproline were prepared by boiling it in aqueous solution with copper carbonate, after first boiling it with a saturated solution of barium hydroxide.

When a solution of δ -bromo- α -benzoylamino- γ -valerolactone in



absolute alcohol is saturated with ammonia, 3-benzoylamino-5-hydroxypiperidone (annexed formula) is obtained, m. p. 225—226°, and this when heated with saturated aqueous barium hydroxide, gives γ -hydroxy- α -benzoylornithine, m. p. 255—256°, of which a monopicate, m. p.

185—190° (compare Kossel and Weiss, A., 1910, ii, 909), and a platinichloride were prepared.

W. G.

Preparation of Cyanamide from Calcium Cyanamide.

EMIL ALPHONSE WERNER (T., 1916, 109, 1325—1327).—Calcium cyanamide is thoroughly kneaded with a little more 50% acetic acid than is required for neutralisation, the paste is exposed to the air for a day until it becomes a dry powder, anhydrous sodium acetate or pumice powder being added if necessary, and then the free cyanamide is extracted with ether. The yield is about 95% of the theoretical.

J. C. W.

Some Reactions Produced by Mercuric Iodide.

ERNALD GEORGE JUSTINIAN HARTLEY (T., 1916, 109, 1302—1305).—Mercuric iodide and acetonitrile do not react when heated together at 100° (compare following abstract), but when methyl iodide is added to the reaction mixture, combination takes place between the three substances, a dark brown, viscous oil being produced. The reaction appears to be a general one, since acetonitrile may be replaced by propionitrile, benzonitrile, phenylacetoneitrile, and β -naphthonitrile. The product appears to be the mercuric iodide of a quaternary base, since when iodine is removed as silver iodide from the acetone solution, and the mercury and excess of silver removed by hydrogen sulphide, a yellow solution of the salt of the base is obtained. No crystalline salts could be obtained, but the addition of sodium hydroxide to the solutions liberates the base as an oil possessing

a strongly alkaline reaction. Various precipitation reactions of solutions of these salts are described.

The mercury compounds could not be obtained pure, but analyses point to one of the two following formulæ: $\text{HgI}_2 \cdot 2\text{RCN} \cdot \text{R}'\text{I}$ or $\text{HgI}_2 \cdot 3\text{RCN} \cdot \text{R}'\text{I}$.

The influence of mercuric iodide in promoting the above reactions has led the author to investigate other reactions. It is found that although no reaction takes place between β -tetramethyl ferrocyanide and methyl iodide when heated at 100° (compare T., 1913, 103, 1199), the addition of mercuric iodide leads to the formation of a mercuri-iodide of hexamethyl ferrocyanogen. T. S. P.

The Reaction between Methyl Iodide and some Metallic Cyanides. ERNOLD GEORGE JUSTINIAN HARTLEY (T., 1916, 109, 1296—1301).—As a result of a fuller examination of the reaction between silver cyanide and methyl iodide (compare Wade, T., 1902, 81, 1608), it is found that these two substances combine slowly at the ordinary laboratory temperature, giving a crystalline compound of the formula $(\text{AgNC})_2 \cdot \text{CH}_3\text{I}$. At a temperature of about 40° , a further molecule of methyl iodide is taken up, and the compound $\text{AgNC} \cdot \text{CH}_3\text{I}$, or perhaps $(\text{AgNC} \cdot \text{CH}_3\text{I})_2$, is formed. Potassium argenticyanide does not react with methyl iodide. The compounds above-mentioned readily undergo decomposition, with the formation of silver iodide and methylcarbylamine.

According to the author, the formulation of potassium argenticyanide and silver cyanide as $\text{K} \cdot \text{N} \cdot \text{C} \cdot \text{N} \begin{smallmatrix} \text{C} \\ \diagup \\ \text{Ag} \end{smallmatrix}$ and $\text{Ag} \cdot \text{N} \cdot \text{C} \cdot \text{N} \begin{smallmatrix} \text{C} \\ \diagup \\ \text{Ag} \end{smallmatrix}$ respectively accounts for the observed phenomena. In the case of silver cyanide, the addition of methyl iodide takes place according

to the scheme: $\text{Ag} \cdot \text{N} \cdot \text{C} \cdot \text{N} \begin{smallmatrix} \text{CH}_3 \\ | \\ \text{I} \end{smallmatrix} \begin{smallmatrix} \text{C} \\ \diagup \\ \text{Ag} \end{smallmatrix}$, which at higher temperatures gives

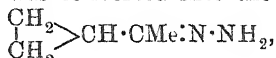
the group $\text{Ag} \cdot \text{N} \cdot \text{C} \begin{smallmatrix} \text{CH}_3 \\ | \\ \text{I} \end{smallmatrix}$, leaving the unsaturated residue $\text{Ag} \cdot \text{N} \cdot \text{C}$ to

combine further with methyl iodide. In the case of potassium argenticyanide, no addition of CH_3I can take place, since the free valencies both of the carbon and nitrogen atoms are no longer available.

When mercuric cyanide and methyl iodide are heated at 110° , a black, tarry, amorphous substance is produced, which cannot be purified. Judging from the weights of the reacting substances, the amorphous substance is the compound $(\text{CH}_3\text{NC})_2 \cdot \text{HgI}_2$. It can also be obtained by the interaction of mercuric iodide and methylcarbylamine; acetonitrile does not react with methyl iodide.

T. S. P.

Isomerisation Phenomena of the Three-membered Ring. N. A. ROZANOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 168—189).—The author has prepared ethylcyclopropane and investigated its transformations. Acetylcyclopropane, prepared from ethyl acetoacetate by way of acetylpropyl alcohol (compare Lipp, A., 1889, 843), was converted into the hydrazone,



b. p. 63·5°/5—6 mm., D_4^{20} 0·9663, n_D^{20} 1·50265. The action of fused potassium hydroxide on the hydrazone in presence of platinised porous tile in a silver tube sealed inside a glass tube at 240—250° yields ethylcyclopropane, b. p. 36—36·5°/750 mm., D_4^{20} 0·6832, n_D^{20} 1·37914 (compare Demjanov and Dojarenko, A., 1913, i, 451; Zelinski and Schtscherbak, A., 1913, i, 254).

When ethylcyclopropane is shaken in a sealed tube at 0° with fuming hydrobromic acid, it is converted into γ -bromopentane, $\text{CH}_2\text{Et}_2\text{Br}$, b. p. 118·5—119·5°/745 mm., D_4^{20} 1·2171, n_D^{20} 1·44299, which, when heated with water in a sealed tube at 100°, gives Δ^2 -pentene and a secondary alcohol. With bromine in direct sunlight, ethylcyclopropane yields: (1) γ -bromopentane, which is a secondary product; (2) $\alpha\gamma$ -dibromopentane, $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CHEtBr}$, b. p. 190—195°/750 mm., D_4^{20} 1·6721, n_D^{20} 1·50482; and (3) apparently a solution of the tetrabromo- in the dibromo-compound. By fuming hydriodic acid it is converted into γ -iodopentane, and the action on it of sulphuric acid diluted with one-half its volume of water gives diethylcarbinol; with dilute nitric acid (D 1·075) it yields ethylmalonic acid.

When passed through a tube containing asbestos and alumina at 300—310°, ethylcyclopropane undergoes isomerisation into Δ^2 -pentene. Reduction of ethylcyclopropane by either Sabatier's or Ipatiev's method readily yields β -methylbutane. In cyclopropane derivatives containing oxygen in one state or another in the side-chain, the trimethylene ring is, however, much more stable, and persists unbroken in the reduction products; thus, reduction of acetylcyclopropane by Ipatiev's method yields cyclopropylmethylcarbinol (compare Michiels, A., 1912, i, 259; Demjanov and Pinegin, A., 1914, i, 527).

The ultra-violet absorption spectra of Δ^2 -pentene, ethylcyclopropane, β -methylbutane, and n -pentane have been investigated. The general absorption of all these hydrocarbons is very weak, and with the unsaturated compounds the absorption is displaced towards the visible part of the spectrum. T. H. P.

Oxidation of *o*-Iodotoluene with Potassium Permanganate. P. J. MONTAGNE (*Chem. Weekblad*, 1916, 13, 1294—1296).—Potassium permanganate oxidises *o*-iodotoluene to a mixture of *o*-iodosobenzoic acid (3 parts) and *o*-iodobenzoic acid (1 part); the iodoso-compound is insoluble in ether. A. J. W.

Additive Compounds of Trinitrobenzene. JOHN JOSEPH SUDBOROUGH (T., 1916, 109, 1339—1348).—In continuation of a study on the additive capacity of polynitro-aromatic compounds

(T., 1901—1911), an account is now given of a large number of compounds of *s*-trinitrobenzene with aromatic hydrocarbons, substitution products of naphthalene, cyclic bases, benzene derivatives, and aromatic sulphur compounds. The hydrocarbons form fairly stable compounds, as they do with picric acid. These are usually yellow, whilst the amines and phenols give more deeply coloured, and frequently more stable, products. It appears, therefore, that the union is due to the latent valencies of the nitro-groups on the one hand and the aromatic nuclei on the other, any hydroxyl, alkyl, keto-, amino-, or alkylamino-groups acting merely as auxochromes and also conferring additional stability on the products. The number of molecules of trinitrobenzene with which one of the molecules combines seems to depend chiefly on the number of aromatic nuclei in the latter, condensed rings acting as one nucleus. Thus compounds like naphthalene, naphthols, quinoline, etc., unite with one molecular proportion of trinitrobenzene; diphenylethane, stilbene, diphenylamine, etc., with two. There are, however, notable exceptions to these generalisations. In some cases the ratio is 1:0.5; in the case of fluorene it is 1:1.5. Reference is also made to the auxochromic effect of amino- and hydroxy-groups and ethylene linkings.

J. C. W.

Additive Compounds of *s*-Trinitrobenzene with Amino-derivatives of Complex Aromatic Hydrocarbons. SHUNKER TRIMBAK CADRE and JOHN JOSEPH SUDBOROUGH (T., 1916, 109, 1349—1354).—As a rule, naphthalene derivatives give more stable additive compounds with trinitrobenzene than the corresponding benzene derivatives. The question therefore arises whether derivatives of still more complex hydrocarbons form still more stable compounds. The behaviour of trinitrobenzene towards 2-, 4-, and 9-aminophenanthrenes, 9-aminoanthracene, the anthramines, the anthrols and their ethyl ethers, 2-aminofluorene, diaminofluorene, and 9-aminoacenaphthene has therefore been examined. Additive compounds of a fair degree of stability are formed in all cases, mostly equimolecular in composition. They are more highly coloured than those of the corresponding naphthalene derivatives, the amines giving brown to black crystals and the hydroxy-compounds reddish-brown. Full descriptions of the substances are given.

J. C. W.

The Sixth (η) Trinitrotoluene and the Corresponding Halogenated Dinitro-substitution Products. W. KÖRNER and A. CONTARDI (*Atti R. Accad. Lincei*, 1916, [v], 25, ii, 339—348. Compare A., 1915, i, 790, 875).—The authors have now prepared the last of the trinitrotoluenes, namely, the 2:3:6-compound, by the following series of transformations: 2:4:6-trinitrotoluene \rightarrow 2:6-dinitro-*p*-toluidine \rightarrow 3-bromo-2:6-dinitro-*p*-toluidine \rightarrow 3-bromo-2:6-dinitrotoluene \rightarrow 2:6-dinitro-*m*-toluidine \rightarrow 2:3:6-trinitrotoluene. Conditions have been found under which 2:4:6-trinitrotoluene gives a 60% yield of 2:6-dinitro-*p*-toluidine; this reaction, and the secondary products of the reduction, are to be dealt with in detail in a later paper.

e*

2:6-Dinitroaceto-*p*-toluidide, $\text{NHAc} \cdot \text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2$, forms slender, white needles, m. p. 223° .

3-Bromo-2:6-dinitro-*p*-toluidine, $\text{NH}_2 \cdot \text{C}_6\text{HMeBr}(\text{NO}_2)_2$, formed, together with a little 3:5-dibromo-2:6-dinitro-*p*-toluidine (*vide infra*), by the action of bromine on the dinitrotoluidine in presence of sodium acetate and acetic acid, crystallises in shining, pale yellow prisms or short needles, m. p. 174° . By means of the diazo-reaction, it may be converted into 3-bromo-2:4:6-trinitrotoluene (compare Bentley and Warren, A., 1890, 485).

3-Bromo-2:6-dinitroaceto-*p*-toluidide, $\text{NHAc} \cdot \text{C}_6\text{HMeBr}(\text{NO}_2)_2$, crystallises in almost colourless plates, m. p. 151° .

3:5-Dibromo-2:6-dinitro-*p*-toluidine, $\text{NH}_2 \cdot \text{C}_6\text{HMeBr}_2(\text{NO}_2)_2$, obtained by further bromination of the corresponding 3-monobromo-derivative (see above), forms shining, pale yellow prisms, m. p. 177° .

3:5-Dibromo-2:6-dinitrotoluene, $\text{C}_6\text{HMeBr}_2(\text{NO}_2)_2$, prepared by treating an absolute alcoholic solution of the previous compound with ethyl nitrite at an excess pressure of about 0.5 atmo., forms shining, white needles or flat plates, m. p. 120° .

3:5-Dibromo-2:4:6-trinitrotoluene, obtained by the action of nitrous vapours at 0° on a suspension of finely powdered 3:5-dibromo-2:6-dinitro-*p*-toluidine in concentrated nitric acid, forms flat, white needles, m. p. 240° ; Palmer (A., 1889, 390) described this as a yellow product, m. p. $229\text{--}230^\circ$.

2:6-Dinitro-*m*-toluidine, $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2$, prepared by the action of 10% alcoholic ammonia solution on 3-bromo-2:6-dinitrotoluene (see below) at 145° , forms shining, pale yellow prisms or needles, m. p. 133.8° .

2:6-Dinitroaceto-*m*-toluidide, $\text{NHAc} \cdot \text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2$, forms shining, thin, colourless plates or large prisms, m. p. 166° .

2:3:6-Trinitrotoluene (η), formed from 2:6-dinitro-*m*-toluidine by way of the diazo-nitrate, crystallises in shining, white needles, belonging to the prismatic class of the monoclinic system [ARTINI: $a:b:c=1.8362:1.03493$; $\beta=56^\circ 39' 5''$], m. p. 111° . By treatment with alcoholic ammonia in a closed tube at $110\text{--}120^\circ$, it is converted into (1) 3:6-dinitro-*o*-toluidine, m. p. 151° , to be described later, and (2) a substance which crystallises in plastic, orange-yellow, flat needles, m. p. 128° , remains unchanged in appearance and melting point after several crystallisations, and is a mixture containing at least 3:6-dinitro-*o*-toluidine and 2:6-dinitro-*m*-toluidine.

3-Chloro-2:6-dinitrotoluene, $\text{C}_6\text{H}_2\text{MeCl}(\text{NO}_2)_2$, forms large, almost colourless, shining prisms, m. p. 75° .

3-Bromo-2:6-dinitrotoluene, $\text{C}_7\text{H}_5\text{O}_4\text{N}_2\text{Br}$, forms slender, white prisms or large prisms, m. p. 86.2° .

3-Iodo-2:6-dinitrotoluene, $\text{C}_7\text{H}_5\text{O}_4\text{N}_2\text{I}$, forms large aggregates of small, shining, colourless plates, m. p. 90° .

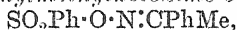
2:3:6-Trinitrobenzoic acid, $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{CO}_2\text{H}$, obtained by oxidising 2:3:6-trinitrotoluene with sulphuric and chromic acids, forms slender, white needles, m. p. $55^\circ (+2\text{H}_2\text{O})$ or 160° (anhydrous).

T. H. P.

Preparation of 4-Nitro-2-aminobenzenesulphonic [3-Nitrosulphanilic] Acid. FARBENFABR. FORM. F. BAYER & Co. (D.R.-P., 294547; from *J. Soc. Chem. Ind.*, 1916, **35**, 1213).—*m*-Nitroaniline is sulphonated at 120–140° with the calculated quantity or a slight excess of fuming sulphuric acid, and the product is cooled and stirred with water. The precipitated sulphonic acid is filtered and washed, and may be purified by means of its sparingly soluble sodium salt. H. W.

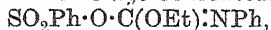
The Beckmann Rearrangement. VI. The Rate of Rearrangement of Phenylmethylketoxime by Different Acid Chlorides, the Spontaneous Rearrangement of its Benzenesulphonic Ester, and the Synthesis of Phenylacetimino Benzenesulphonate. MITSURU KUHARA and HIKOHEI WATANABE (*Mem. Coll. Sci. Kyoto*, 1916, **1**, 349–353. Compare A., 1915, i, 143).—As in the case of benzophenone-oxime, so with the oxime of acetophenone, the chlorides of the stronger acids effect rearrangement more quickly than those of the weaker acids. The yield of acetanilide obtained by heating the oxime with acyl chlorides is found to vary, for example, from only 39% at the end of six hours with acetyl chloride to 98·8% during half an hour with benzenesulphonyl chloride.

Correspondingly, *phenylmethylketoxime benzenesulphonate*,



colourless needles, m. p. 60–61°, spontaneously changes into a viscous oil in a few days in the cold, quickly in ultra-violet light, or with violence at 81–82°. This oil is *phenylacetimino benzenesulphonate*, $\text{SO}_2\text{Ph}\cdot\text{O}\cdot\text{CMe}:\text{NPh}$, which may also be prepared by the interaction of phenylacetimino chloride and silver benzenesulphonate. J. C. W.

The Beckmann Rearrangement. VII. The Rearrangement of Ethylsynbenzhydroximic Acid, the Different Acid Chlorides, and its Benzenesulphonic Ester. MITSURU KUHARA and FUSAO ISHIKAWA (*Mem. Coll. Sci. Kyoto*, 1916, **1**, 355–360).—Ethylsynbenzhydroximic acid follows the same rule as the ketoximes, namely, that the chlorides of stronger acids bring about its rearrangement more readily than those of weak acids. The *benzenesulphonate*, $\text{SO}_2\text{Ph}\cdot\text{O}\cdot\text{N}:\text{CPh}\cdot\text{OEt}$, has m. p. 54–55°, and decomposes on heating, violently at 150°, into phenylcarbimide and ethyl benzenesulphonate. The expected intermediate product, *ethoxyphenyliminomethyl benzenesulphonate*,



is therefore unstable at higher temperatures, but it can be isolated as an oil if the original oxime is warmed with benzenesulphonyl chloride in dry pyridine. J. C. W.

Biological Syntheses: *p*-Hydroxyphenylethanol (Tyrosol). P. S. PISCHTSCHIMUKA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1–54). The greater part of this paper has been already published (compare A., 1912, ii, 590; Ehrlich and Pischtschimuka, A., 1912, i, 853).

The formation of esters during the normal alcoholic fermentation of amino-acids appears to be a biological process of wide extent, its object being the union of the excess of acids and alcohols, which would be injurious to the micro-organisms. A number of the esters of tyrosol have now been prepared by ordinary chemical synthetical methods, and are found to exhibit faint odours at the most. The mixture of esters formed naturally during alcoholic fermentation has a pleasant odour, but this is probably due to the presence of admixed indole derivatives. The following esters have been prepared.

The *monoacetate*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OAc}$, forms thick, prismatic, non-hygroscopic crystals, m. p. 59° , and is very sparingly soluble in cold water, although the solution gives Millon's reaction. The *diacetate*, $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OAc}$, forms a transparent, colourless, viscous oil, b. p. $187^\circ/18 \text{ mm.}$, solidifying to a vitreous mass at the temperature of liquid air; it is almost insoluble in water, but the aqueous solution gives Millon's reaction. The *monoisovalerate*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHMe}_2$, forms a colourless, oily liquid, b. p. $208.5^\circ/18 \text{ mm.}$, with a faint, aromatic odour. The *diisovalerate*, $\text{C}_{18}\text{H}_{26}\text{O}_4$, is a liquid, b. p. $228^\circ/18 \text{ mm.}$, resembling the monoisovalerate, and forms a stable emulsion with water. The *monoformate*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CHO}$, does not distil even at 12 mm. pressure, and does not crystallise. The *succinate*, $(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2)_2 \text{C}_4\text{H}_4\text{O}_4$, crystallises in slender needles, m. p. 116° . The *hydrogen succinate*,

$\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, forms crystals, m. p. 106° , gives an intense Millon's reaction, and has an acid reaction towards phenolphthalein. The *tartrate*, $(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2)_2 \text{C}_4\text{H}_4\text{O}_6$, forms colourless, prismatic aggregates, m. p. 143° . The *hydrogen tartrate*,

$\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot [\text{CH}(\text{OH})]_2 \cdot \text{CO}_2\text{H}$, forms crystals, m. p. 162° , is comparatively stable towards water, and yields a crystalline *sodium salt*. T. H. P.

Esterification. VIII. The Esterification of Benzoic Acid by Isomeric Butyl Mercaptans. J. W. KIMBALL and E. EMMET REID (*J. Amer. Chem. Soc.*, 1916, **38**, 2757—2768).—The four isomeric butyl thiolbenzoates were prepared by the action of the corresponding butyl bromide on the potassium salt of thiolbenzoic acid. *n-Butyl thiolbenzoate* has b. p. $160^\circ/23 \text{ mm.}$, $D_{20}^{25} 1.0514$; *isobutyl thiolbenzoate*, b. p. $150^\circ/20 \text{ mm.}$, $D_{20}^{25} 1.0457$; *sec-butyl thiolbenzoate*, b. p. $151^\circ/23 \text{ mm.}$, $D_{20}^{25} 1.0488$; and *tert-butyl thiolbenzoate*, b. p. $110^\circ/28 \text{ mm.}$, $D_{20}^{25} 1.0468$.

The authors have determined the rates and limits of esterification of benzoic acid by normal, *iso*-, and *sec*-butyl mercaptans at 200° , and also the limits for the saponification of the four butyl thiolbenzoates at the same temperature. In the esterifications, the rates and limits for the normal and *iso*-mercaptans were found to be practically the same, those for the secondary mercaptans being much lower. In every case the limits were much lower than those

for the corresponding alcohols, and were independent of the relative amounts of acid and mercaptan used. The saponification of the esters was found to be very irregular and unsatisfactory on account of the immiscibility of the ester and water and the decomposition of the esters, particularly in the case of *tert*-butyl thiolbenzoate.

W. G.

Esterification. VII. The Esterification of *o*-, *m*-, and *p*-Toluic Acids by Ethyl Mercaptan. J. H. SACHS and E. EMMET REID (*J. Amer. Chem. Soc.*, 1916, **38**, 2746—2757).—A quantitative study of the esterification of the three toluic acids by ethyl mercaptan and of the hydrolysis of ethyl *o*- and *p*-thiol-toluates by water.

o-Thioltoluic acid, b. p. 133°/35 mm., D_{25}^{25} 1.1451, was obtained in the form of its *potassium* salt by adding *o*-toluoyl chloride to an alcoholic solution of potassium hydroxide saturated with hydrogen sulphide. The potassium salt when alkylated with ethyl bromide gave *ethyl o*-thioltoluate, $C_6H_4Me \cdot CO \cdot S Et$, b. p. 133°/15 mm., D_{25}^{25} 1.0513. *p*-Thioltoluic acid, b. p. 131°/15 mm., m. p. 43.5—44°, gave *ethyl p*-thioltoluate, b. p. 150°/18 mm., D_{25}^{25} 1.0708. The meta-acid and thiol ester were not prepared. The three toluic acids were separately heated in sealed tubes with ethyl mercaptan at 200° for one, two, four, eight, and sixteen days, and in each case the percentage of acid esterified was determined and the velocity constants calculated, using the formula for a bimolecular reaction. Ethyl *o*- and *p*-thioltoluates were similarly heated with water, and the percentage of ester saponified and the velocity constant determined. The three acids show the same relations as to velocities and limits of esterification with ethyl mercaptan as they do with ethyl alcohol, the limits being, however, much lower with the mercaptans than with the alcohols. The limit of esterification is in each case independent of the proportions of acid and mercaptan used, the three acids reaching practically the same limits of esterification under the above treatment.

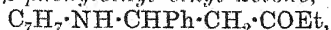
W. G.

The Synthesis of Amino-acids. Allylhippuric Acid. S. L. P. SØRENSEN (*Compt. rend. Lab. Carlsberg*, 1916, **11**, 212—222).—A more detailed account of work already published (compare A., 1908, i, 981).

W. G.

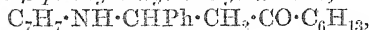
Formation and Properties of β -Amino-ketones derived from Aromatic Imines. CHARLES MAYER (*Bull. Soc. chim.*, 1916, [iv], **19**, 427—432. Compare A., 1904, i, 832; 1905, i, 214, 357).—Other ketones than methyl ketones can be condensed with imines to give β -amino-ketones. In this way, benzylidene-*m*- and *p*-toluidines have been condensed with certain ketones.

Benzylidene-*p*-toluidine when condensed with methyl ethyl ketone gives β -*p*-toluidino- β -phenylethyl ethyl ketone,



m. p. 156°. When this is dissolved in concentrated sulphuric acid or glacial acetic acid, and the solution poured on ice, styryl

ethyl ketone is obtained. A similar decomposition is produced if the ketone is warmed with acetyl chloride, benzoyl chloride, or phenylcarbimide. β -m-Toluidino- β -phenylethyl ethyl ketone, m. p. 127° , when warmed with phenylhydrazine hydrochloride gives phenylbenzylidenehydrazine, methyl ethyl ketone, and *m*-toluidine hydrochloride. With methyl hexyl ketone, benzylidene-*p*-toluidine gives β -*p*-toluidino- β -phenylethyl hexyl ketone,



colourless needles, m. p. 85° , which by the action of sulphuric acid or when warmed in alcoholic solution with a few drops of pyridine gives cinnamenyl hexyl ketone. β -m-Toluidino- β -phenylethyl nonyl ketone, $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_9\text{H}_{19}$, felted needles, m. p. 72° , is decomposed by sulphuric acid, giving cinnamenyl nonyl ketone.

o-Hydroxybenzylideneaniline condenses very slowly with methyl ethyl ketone, giving β -aminino- β -*o*-hydroxyphenylethyl ethyl ketone, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{NHPh})\cdot\text{CH}_2\cdot\text{COEt}$, m. p. 232° , which when boiled in benzene solution with a few drops of pyridine gives a compound, m. p. 184° . With concentrated sulphuric acid, the ketone gives a violet-coloured compound, m. p. 130° (decomp.). W. G.

Isomerisation, Polymerisation, and Formation of Additive Products of α -Pinene. H. J. PRINS (*Chem. Weekblad*, 1916, **13**, 1264—1276).—On warming a solution of levorotatory α -pinene in glacial acetic acid at 60 — 70° with 5% of phosphoric acid (D 1.7), *l*-limonene is formed, with development of heat. Strong mineral acids, and aluminium, ferric, and zinc chlorides convert α -pinene into a product resembling colophony. α -Pinene combines with water, alcohol, and organic acids, forming alcoholic derivatives of the borneol or terpineol type. A. J. W.

Isomeric Sabinols. VINCENZO PAOLINI and GIOVANNI REBORA. (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 377—381. Compare A., 1911, i, 730; 1912, i, 635).—Discordant values have been given by different investigators for the physical constants of sabinol, but no attempt seems to have been made to separate stereoisomeric modifications. The authors have prepared from savin oil a hydrogen phthalate of sabinol, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{15}$, which recrystallises in tufts of white, silky needles, m. p. 95° , $[\alpha]_D^{20}$, $-14^{\circ}63'$ (in methyl alcohol). Hydrolysis of this ester yields sabinol, b. p. 208° , D_4^{20} 0.9518, n_D^{20} 1.4895, $[\alpha]_D^{20}$ $+7^{\circ}56'$, and treatment of the sabinol with phthalic anhydride yields solely the hydrogen phthalate just described. These two compounds appear to be definite chemical individuals.

That savin oil contains no other isomeric sabinol has been shown in the following manner. The uncrystallisable syrup obtained after removal of the solvent from the mother liquors of the hydrogen phthalate was converted into the strychnine salt, which, when crystallised several times and hydrolysed with cold, dilute hydrochloric acid, gave only the acid phthalate described above. *Strychnine sabinol phthalate*, $\text{C}_{30}\text{H}_{40}\text{O}_6\text{N}_2$, crystallises in shining, white needles, m. p. 200 — 201° . T. H. P.

Theory of Vegetable Tanning. HENRY RICHARDSON PROCTER and JOHN ARTHUR WILSON (T., 1916, 109, 1327—1331).—A theoretical paper, the results being based on previously published work. It is shown that the combination of tannins and hide fibre, and the effect of acids and neutral salts in the tanning process, are explained by the existence of "membrane potentials," as described by Donnan (A., 1911, ii, 848). Equations are given with regard to the relation of the various concentrations involved, which equations should also be applicable to dyeing processes.

T. S. P.

Saponification of 2:5-Dimethylfuran-3:4-dicarboxylic Ester at 50°. G. KORSCHUN and A. GOUNDER (*Bull. Soc. chim.*, 1916, [iv], 19, 426; *J. Russ. Phys. Chem. Soc.*, 1916, 48, 690—691).—A molecule of the ester was treated with four molecules of potassium hydroxide in dilute solution, the results indicating that the process is one of saponification of the acid ester of the dicarboxylic acid.

W. G.

Preparation of 2:3-Diketodihydrothionaphthens. R. STOLLÉ (D.R.-P., 291759; addition to D.R.-P., 281046; from *J. Soc. Chem. Ind.*, 1916, 35, 1213).—2:3-Diketodihydrothionaphthens, $C_6H_3R \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ S \end{smallmatrix} CO$, are obtained by treating aromatic mercaptans with oxalyl chloride and subjecting the resulting chlorides, $R \cdot S \cdot CO \cdot COCl$, to the action of condensing agents. *Methyl-2:3-diketodihydrothionaphthen*, glistening, yellowish-red leaflets, m. p. 144°, is obtained in this way from *p*-thiocresol.

H. W.

(A) Cephaeline isoButyl Ether and (B) Cephaeline Propyl Ether and Salts Thereof. J. W. MEADER (Brit. Pats. (A), 1915, 11717 and (B) 11719; from *J. Soc. Chem. Ind.*, 1916, 35, 1271).—*Cephaeline isobutyl ether* is produced by treating cephaeline with an alkali metal and an isobutyl haloid, for example, from isobutyl bromide, cephaeline, and a solution of sodium ethoxide in absolute alcohol. It is a varnish-like substance, easily soluble in alcohol, ether, or chloroform. It forms a crystalline *hydrobromide*, white needles, and *hydrochloride*.

Cephaeline propyl ether is similarly prepared, and resembles the isobutyl compound.

H. W.

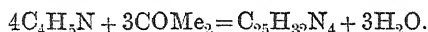
Process of the Condensation of Pyrrole with Acetone. V. V. TSHELINCEV and B. V. TRONOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 105—127. Compare A., 1915, i, 990).—The condensation of pyrrole with acetone, which has been studied by von Baeyer, Dennstedt, and others, is a complex process, and the authors have now studied it in various media with the object of obtaining the intermediate as well as the final products.

In acetone, this condensation yields about equal proportions of: (1) The crystalline compound, $C_{23}H_{36}N_4$, m. p. 290—292, obtained by von Baeyer (A., 1886, 1043) and by Dennstedt and Zimmermann (A., 1887, 598, 1052); after several crystallisations from

acetone and alcohol and from benzene, the compound melts at 296° . (2) An amorphous compound, $C_{28}H_{36}ON_4$, m. p. above 180° (decomp.), which has the normal molecular weight in freezing benzene, but could not be obtained crystalline; when its solution is left in contact with the air, it undergoes gradual transformation into a compound which begins to decompose at about 230° , and gives analytical results in approximate correspondence with the ratios $C_{28}:H_{34}:O_6:N_4$, but was not obtained pure.

In alcohol, the condensation yields, in the cold, both the above products, but, in the hot, almost exclusively the crystalline compound (1).

In an aqueous medium containing a little hydrochloric acid and just sufficient acetone to dissolve the pyrrole used, the condensation gives, at the ordinary temperature, only a very small proportion of the crystalline compound, m. p. 290 — 292° , the preponderating product being the compound, $C_{25}H_{32}N_4$, which forms a solid, non-crystalline mass, has the normal molecular weight in freezing benzene, and is formed according to the equation



Oxidation of this compound by means of the air yields: (1) a pink, powdery compound, $C_{28}H_{36}ON_4$, m. p. 152 — 154° , having the normal molecular weight in freezing bromoform; (2) a bright orange, amorphous, flocculent compound, $C_{28}H_{36}O_3N_4$, which begins to melt at about 92 — 95° , then decomposes without completely melting, and gives off gas at 115° ; its cryoscopic behaviour in bromoform is normal; (3) an amorphous compound, $C_{28}H_{34}O_6N_4$ (?), which begins to decompose at 230° . The compound, $C_{25}H_{32}N_4$, is converted almost quantitatively into the crystalline compound, m. p. 290 — 292° , when heated with hydrochloric acid in presence of acetone.

The condensation of pyrrole with acetone takes place also in presence of nitric or sulphuric acid or sulphur dioxide, and, although far more slowly, in that of hydrogen sulphide; potassium hydroxide is without influence in this direction. The ordinary organic acids also bring about the condensation, which in this case yields: (1) the crystalline compound, m. p. 290 — 292° , and (2) a compound, $(C_{28}H_{36}ON_4)_3$, which forms small, pink crystals, beginning to decompose at 160° , and in freezing bromoform has the molecular weight corresponding with the trebled formula; when boiled with hydrochloric acid, this compound undergoes resinification and conversion into the crystalline product, m. p. 290 — 292° .

The latter compound and that now obtained by the authors, $C_{28}H_{32}N_4$, are of the same order of complexity as the natural pyrrole pigments, chlorophyll and hæmin, each of these consisting of four pyrrole nuclei. That not more than four nuclei are concerned in these condensations under both natural and artificial conditions is regarded as the result of stereochemical relations.

T. H. P.

Structure of the Condensation Products of Pyrrole and Acetone. V. V. TSCHELINCEV and B. V. TRONOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 127—155. Compare preceding abstract).—To the two condensation products already described are given the names: $C_{25}H_{32}N_4$, "tetrapyrrole-triacetone condensation product," and $C_{28}H_{36}N_4$, "tetrapyrrole-tetra-acetone condensation product." The former is converted almost quantitatively into the latter when heated with acetone in presence of hydrochloric acid. The close relation of these two condensation products to etioporphyrin is shown by the fact that, on oxidation, they yield maleimide, whereas etioporphyrin gives a substituted maleimide.

The conclusions which have been drawn concerning the molecular configuration of these condensation products are based principally on their behaviour when distilled in the dry state and when treated with sodium alkoxide. Recent work on pyrrole has, however, indicated that such conclusions are unwarranted, since, at a high temperature, complex molecular decompositions and reconstructions are known to occur, and the action of sodium alkoxide takes place as well at the linkings between the pyrrole nuclei as at the free 2- and 3-positions of these nuclei. The question of the structures of these condensation products remains therefore open, and the following experiments have been made with a view to its elucidation.

When treated with magnesium propyl iodide, these condensation products (1 mol.) yield respectively 3.94 and 4.12 mols. of gas, so that it may be assumed with safety that, in each case, the four imino-groups of the pyrrole residues remain unchanged. Further, in ethereal solution, the organo-magnesium compounds formed with magnesium propyl iodide absorb carbon dioxide, giving products which, when decomposed, yield the absorbed carbon dioxide and the unchanged original compounds. This behaviour is as would be expected of compounds of the carbamic acid type, and confirms the fact that the magnesium residue replaces the iminic hydrogen.

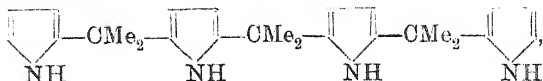
Dennstedt's statement that 1-substituted derivatives of pyrrole do not undergo condensation with acetone may possibly be true in some instances, but is not of general application. With 1-methylpyrrole, indeed, acetone condenses with moderate readiness, although not so energetically as with pyrrole itself. The compound obtained, $(C_{32}H_{42}N_4)_3$, forms crystals, m. p. 153—155°, and in freezing benzene has the molecular weight corresponding with the trebled formula. That the imino-group does not participate in the condensation with acetone is therefore confirmed.

When oxidised in acetic acid solution by means of chromic acid, both the tetrapyrrole-triacetone and the tetrapyrrole-tetra-acetone condensation products yield unsubstituted maleimide. It is evident, therefore, that the condensation does not involve removal of the hydrogen atom in the 3- or 4-position of the pyrrole nucleus.

The conclusion is drawn that the union of the pyrrole with the acetone in these condensation products takes place solely at the

2-positions of the nuclei. From the fact that dry distillation of the tetrapyrrole-tetra-acetone product yields a decomposition product with condensed acetone molecules indicates the possibility of the existence of the acetone in a condensed form in the condensation products. Experiment shows that the condensation of mesityl oxide and pyrrole in alcoholic solution in presence of hydrochloric acid yields a *compound*, $C_{32}H_{42}O_5N_4$ (?), m. p. about 170° (decomp.), quite different in type from those given by acetone and pyrrole under similar conditions.

These considerations lead to the formula



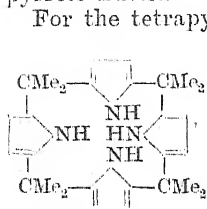
for the tetrapyrrole-triacetone condensation product, and in the tetrapyrrole-tetra-acetone product the free hydrogen atoms of the two CH-groups in the 2-positions of the terminal pyrrole nuclei are eliminated, and the corresponding carbon atoms united by way of a CMe_2 -group. The probable accuracy of this relation between the two compounds is shown by the fact that the more complex is obtained in 90% yield when the simpler one is heated for five minutes on a water-bath in alcoholic solution with acetone and a little hydrochloric acid.

Towards hydroxylamine (compare Ciamician and Zanetti, A., 1890, 264, 1155; 1891, 1502; Fischer and Zimmermann, A., 1914, i, 318), the two condensation products exhibit widely varying behaviour. Even on prolonged boiling no action takes place with the tetra-acetone compound, but the tetrapyrrole-tetra-acetone condensation product readily yields a *compound*, $C_{35}H_{50}O_5N_4$ (?), which forms an amorphous, brownish-yellow powder, and undergoes oxidation with such facility that its accurate investigation is impossible. Fischer and Zimmermann (*loc. cit.*) studied the action of hydroxylamine on bilirubin, hæmin, porphyrinogen, etc., and obtained similarly unsatisfactory results.

Each of the two condensation products was treated with magnesium ethyl bromide, and the resultant products then subjected to the action of acetic anhydride. Under this treatment, the tetrapyrrole-tetra-acetone condensation product gave a very small proportion of a bright red compound, the bulk of the original substance remaining unchanged. The tetrapyrrole-triacetone condensation product gave, however, a good yield of a bright red, amorphous *compound*, $C_{45}H_{60}O_5N_4$ (?), whereas simple acetylation at the imino-groups should give a compound of the formula $C_{33}H_{40}O_4N_4$. The slight reactivity of the tetrapyrrole-tetra-acetone compound is regarded as due to its cyclic structure and to the absence of the highly active 2-hydrogen atoms of the pyrrole nucleus.

The action of hydriodic acid on chlorophyll or hæmin yields hæmopyrrole, the links connecting the pyrrole nuclei being broken, with formation of this very simple pyrrole derivative. Fischer and Bartholomäus (A., 1913, i, 209), who applied this action to definite

condensation products of pyrrole compounds with aldehydes and ketones, found that compounds of this type with side-chains in the 2-position, such as hæmin, break down in about two hours, whereas those with side-chains in the 3-position require for their resolution fourteen to sixteen hours at the boiling point. When a solution of the tetrapyrrole-triacetone condensation product in concentrated acetic acid is heated with hydriodic acid, or a solution of the tetrapyrrole-tetra-acetone product in a mixture of benzene and alcohol with hydrochloric acid, for one and a-half hours on a water-bath, a large proportion of an oily, resinous product, giving a green coloration with alkali hydroxide, is formed in either case. If, however, the period of heating is restricted to four to five minutes, in the first instance 44%, and in the second instance 45%, of the condensation product taken is converted into the other; the former transformation also takes place, although far more slowly, if the hydriodic acid is replaced by acetic acid. These results support the conclusion that the dimethylmethylethylene chains of these compounds are linked to the 2-positions of the pyrrole nuclei.



For the tetrapyrrole-tetra-acetone condensation product, a structure of the type of the annexed formula is proposed, this being analogous to Küster's formula for hæmin. Willstätter's objection to the latter on the ground that it contains a 16-membered ring, is discussed, and it is shown that the value of the "tension" in the closed ring of the authors' formula just given is small under any supposition, and, according

to one arrangement, zero.

T. H. P.

Saponification of some Pyrrolemonocarboxylic and Pyrroledicarboxylic Esters at a Temperature of 98.3—98.7°. G. KORSCHUN and A. GOUNDER (*Bull. Soc. chim.*, 1916, [iv], 19, 407—426; *J. Russ. Phys. Chem. Soc.*, 1916, 48, 667—690).—These measurements made at the higher temperature confirm the results already obtained at 50°, and, to a certain extent, some of the conclusions previously drawn (compare A., 1916, ii, 525).

W. G.

Preparation of Vinyl-diacetoneamine [2:2:6-Trimethyl-4-piperidone] and its Salts. A. T. KING, F. A. MASON, and S. B. SCHRYVER (*Brit. Pat.*, 101738; from *J. Soc. Chem. Ind.*, 1916, 35, 1235).—The action of an acetal of the type $\text{CH}_3\cdot\text{CH}(\text{OR})_2$ with diacetoneamine or its salts, or with acetone saturated with ammonia, produces 2:2:6-trimethyl-4-piperidone or its salts according to the equation $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NH}_2 + \text{CH}_3\cdot\text{CH}(\text{OR})_2 =$
 $\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NH}\cdot\text{CMe}_2 + 2\text{ROH}$. Better yields (about 90% of the theoretical) are obtained in much shorter times than by previously published methods. Thus, the oxalate is obtained by heating

diacetoneamine hydrogen oxalate with diethylacetal in solution in normal butyl alcohol for three hours or in ethyl alcohol for seven hours. H. W.

Combination of Organic Acids [Salicylic Acid and 2-Phenylquinoline-4-carboxylic Acid]. ELI LILLY & CO. (U.S. Pat., 1916, 1203499, and Brit. Pat., 1916, 102136; from *J. Soc. Chem. Ind.*, 1916, **35**, 1272).—A compound of salicylic acid and 2-phenylquinoline-4-carboxylic acid is produced by precipitating an equimolecular mixture of their alkali salts with a mineral acid.

H. W.

Combination of Organic Acids [Ester of 2-Phenylquinoline-4-carboxylic Acid and Salicylic Acid]. ELI LILLY & CO. (U.S. Pat., 1203500; from *J. Soc. Chem. Ind.*, 1916, **35**, 1272. Compare preceding abstract).—An ester of salicylic acid and 2-phenylquinoline-4-carboxylic acid, $C_9H_5NPh \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2H$, is prepared by treating 2-phenylquinoline-4-carboxylic acid with thionyl chloride and combining the resulting chloride with salicylic acid.

H. W.

2-Naphthylquinoline-4-carboxylic Acids. CHEM. FABRIK AUF AKTIEN FORM. E. SCHERING (U.S. Pat., 1197462; from *J. Soc. Chem. Ind.*, 1916, **35**, 1272).—2-Naphthylquinoline-4-carboxylic acids are prepared by condensing isatin with naphthyl methyl ketone in alkaline solution, or by condensing aniline with pyruvic acid and naphthaldehyde. For example, a solution of isatin (180 parts) in alcohol (500 parts) and potassium hydroxide solution (33%, 300 parts) is heated with α -naphthyl methyl ketone (90 parts) on the water-bath for some hours. After removal of alcohol, the product is precipitated by hydrochloric acid, redissolved in sodium carbonate solution, again precipitated, and crystallised from dilute alcohol. 2- α -Naphthylquinoline-4-carboxylic acid forms yellowish-red needles, m. p. 198°; 2- β -naphthylquinoline-4-carboxylic acid, yellow crystals, has m. p. 234°. Both acids are remedies for gout and rheumatism.

H. W.

Action of the Grignard Reagent on Cyanogen Compounds. Synthesis of Amidines from Cyanamides. ROGER ADAMS and C. H. BEEBE (*J. Amer. Chem. Soc.*, 1916, **38**, 2768—2772).—Dibenzylcyanamide, when acted on with magnesium alkyl and aryl haloids, gives additive compounds which on decomposition yield the salts of substituted amidines. These salts are not easy to purify, owing to their solubility and their tendency to become coloured during crystallisation, it being necessary in one case to prepare the carbamide by the action of phenylcarbimide on the free amidine. The amidines themselves are mostly oils or very soluble solids with low melting points. The following compounds were prepared.

Dibenzylpropenylamidine hydrochloride,
 $\text{N}(\text{CH}_2\text{Ph})_2 \cdot \text{C}(\text{Et})\text{:NH}, \text{HCl}$,
 rhombohedra, m. p. 204—204.5°.

Dibenzylbenzamidine hydrochloride,
 $\text{N}(\text{CH}_2\text{Ph})_2 \cdot \text{C}(\text{Ph})\text{:NH}, \text{HCl}$,
 rhombohedra, m. p. 211.5°. *Dibenzylbenzamidine* is a white solid,
 m. p. 70—71°.

Dibenzyl-p-tolenylamidine hydrochloride,
 $\text{N}(\text{CH}_2\text{Ph})_2 \cdot \text{C}(\text{C}_6\text{H}_4\text{Me})\text{:NH}, \text{HCl}$,
 always contained a certain amount of a yellow impurity, but yielded
dibenzyl-p-tolenylamidinephenylcarbamate,
 $\text{N}(\text{CH}_2\text{Ph})_2 \cdot \text{C}(\text{C}_6\text{H}_4\text{Me})\text{:N} \cdot \text{CO} \cdot \text{NHPh}$,
 slender, white needles, m. p. 158°. W. G.

The Molecular Rearrangement of Triarylmethylazides.
 JAMES KUHN SENIOR (*J. Amer. Chem. Soc.*, 1916, **38**, 2718—2726).
 —Triphenylmethylazide, when heated in a sealed tube at 225° for
 one hour, undergoes molecular rearrangement, giving phenylimino-
 benzophenone, $\text{CPh}_3 \cdot \text{N}_3 \rightarrow \text{CPh}_3 \cdot \text{N} + \text{N}_2 \rightarrow \text{CPh}_2 \cdot \text{N} \cdot \text{Ph} + \text{N}_2$.

When *p*-chlorotriphenylmethyl chloride (compare Gomberg,
 A., 1904, i, 658, 988) is boiled with hydrazine hydrate in absolute
 ether, the main product is either *p*-chlorotriphenylmethyl-
 hydrazine hydrochloride, m. p. 122°, or *bis-p*-chlorotriphenyl-
 methylhydrazine, m. p. 201°, according to the proportions of the
 reagent used. When this hydrazine hydrochloride is boiled in
 alcoholic solution with 7% hydrochloric acid, *p*-chlorotri-
 phenylmethylazide is obtained as a gum, which when heated at
 215° undergoes rearrangement, giving phenyliminobenzopheno-
 none and chlorophenyliminobenzophenone in the molecular pro-
 portion of 68.1 to 31.9, these figures being in close agreement with
 those obtained by Leech for *p*-chlorotriphenylmethylhydroxyl-
 amine (compare A., 1914, i, 268). W. G.

**The Molecular Rearrangement of *sym*-Bistriarylmethyl-
 hydrazines.** JULIUS STIEGLITZ and JAMES KUHN SENIOR (*J. Amer.*
Chem. Soc., 1916, **38**, 2727—2736. Compare preceding abstract).
 —All attempts to cause a rearrangement of hydrazines by the loss
 of ammonia through treatment with concentrated acids or zinc
 chloride were unsuccessful. Attempts were then made to cause a
 rearrangement of *sym*-bistriarylmethylhydrazines, and these were
 successful, the hydrazines being heated with zinc chloride at 300°
 for ten minutes. Under these conditions, bistriphenylmethyl-
 hydrazine, $\text{CPh}_3 \cdot \text{NH} \cdot \text{NH} \cdot \text{CPh}_3$, gave aniline and triphenylmethane,
 the formation of aniline being due to migration of a phenyl group
 from carbon to nitrogen. *Bis-p*-chlorotriphenylmethylhydrazine
 undergoes the same rearrangement, giving aniline and, in all
 probability, *p*-chloroaniline. The mechanism of the action is not
 yet clear, as it does not proceed smoothly. A number of attempts
 were made to rearrange unsymmetrical hydrazines and hydrazones,
 but they were all unsuccessful. W. G.

Preparation of Collargol. A. F. GERASIMOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 87—90, 251—253).—Investigations on the preparation of collargol by Paal's method (A., 1902, i, 653; ii, 500) show that the reduction to metallic silver takes place mainly, if not entirely, at the expense of the silver oxide, preparations with approximately the same proportion of silver being obtained with widely varying concentrations of silver nitrate. The percentage of silver in the preparations is increased but slightly by precipitation with acids.

On the basis of these results, the following method of obtaining collargol is recommended. The reducing mixture is prepared by shaking 100 grams of albumin with a solution of 15 grams of sodium hydroxide in 500 c.c. of water until it is uniformly distributed throughout the liquid, which is then heated for about an hour on a water-bath and freed from a little flocculent precipitate by filtration. To 27—30 grams of this solution is added the silver oxide obtained by precipitating a solution of 10 grams of silver nitrate with potassium hydroxide and washing five times by decantation. The mixture is diluted to about 200 c.c. and heated on a water-bath, with constant shaking, for forty to sixty minutes. When cold, the liquid is precipitated with a few drops of concentrated acetic acid, and the precipitate washed five or six times and dissolved in water in presence of a minimal quantity of sodium hydroxide. The liquid is allowed to settle, and dried either in a desiccator over sulphuric acid or in a vacuum at about 40°, or in a current of air free from dust; over-drying should, however, be avoided. In this way, a blue powder containing about 75% of silver is obtained.

T. H. P.

Protein Copper Compounds. THOMAS B. OSBORNE and CHARLES S. LEAVENWORTH (*J. Biol. Chem.*, 1916, **28**, 109—123).—On adding copper sulphate solution to an alkaline solution of edestin or gliadin, a blue copper protein compound is precipitated of variable composition, which is insoluble in excess of the copper sulphate. When kept, the colour of the precipitate changes to brown, due to decomposition, with liberation of partly dehydrated copper hydroxide. The authors suggest that the copper unites with the imino-nitrogen of the $R \cdot CO \cdot NH \cdot R$ groups.

H. W. B.

Antigenic Properties of β -Nucleoproteins. H. GIDEON WELLS (*J. Biol. Chem.*, 1916, **28**, 11—16).—The nucleoproteins extracted from tissues by cold water, dilute salt, or weak alkaline solutions lose their antigenic properties on being heated at 100°. The so-called β -nucleoproteins, however, which are obtained from various tissues by extracting with boiling water, possess definite antigenic properties demonstrable by the anaphylactic reaction. Judging from the degree of anaphylaxis produced, the β -nucleoproteins from the pancreas and spleen of the ox and from the pancreas of the pig, seem to be similar, but not identical.

H. W. B.

Rotatory Power of Nucleic Acids and of Nucleates of the Alkali Metals. M. A. RAKUZIN and (MLLE.) EK. MAK. BRAUDO (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 97—99. Compare Rakuzin and Logunova, A., 1915, i, 1017).—Measurement of the rotation of Parke, Davis, & Co.'s 5% nucleic acid solution gives the value $[\alpha]_D +68.51^\circ$ for the specific rotation of the nucleic acid. Dilute nucleic acid solutions were neutralised towards phenolphthalein by means of decinormal alkali hydroxide solutions, and the rotatory powers of the alkali nucleates thus obtained then measured, the values of $[\alpha]_D$ being: lithium salt, $+21.73^\circ$; ammonium, $+24.77^\circ$; sodium, $+29.58^\circ$; and potassium, $+35.39^\circ$. Thus, just as with the caseinogenates, the specific rotation of the alkali nucleates increases with the atomic weight of the metal. The rotations of the nucleates are, however, less than that of the nucleic acid, whereas caseinogenates give higher rotations than caseinogen.

T. H. P.

The Significance of Electrolytes in Processes of Imbibition. WOLFGANG OSTWALD (*Biochem. Zeitsch.*, 1916, **77**, 329—332).—The differences between the results obtained by the author and those of Lenk (A., 1916, i, 346) on the influence of salts on the imbibition of water by gelatin are due to the fact that the author worked with nearly dry plates of the material, whereas Lenk worked with plates which had already imbibed 80—85% of water. The latter was therefore only investigating the action of salts on an intermediate stage of the imbibition process, whereas the author had ascertained their action on the final equilibrium and on the whole course of the imbibition. S. B. S.

Influence of Acetic Acid on the Synthesising and Hydrolysing Properties of β -Glucosidase. EM. BOURQUELOT and A. AUBRY (*J. Pharm. Chim.*, 1916, [vii], **14**, 359—363. Compare A., 1915, i, 604).— β -Glucosidase is more resistant to the injurious action of acetic acid than is α -glucosidase, synthesis taking place almost normally up to a content of 0.1% of acetic acid. Higher concentrations of acetic acid retard the synthesis, owing to the progressive destruction of the enzyme. Similar results were obtained in studying the hydrolysing action of the enzyme in the presence of acetic acid.

W. G.

Physiological Chemistry.

Relation between the Water and the Dextrose Concentration of the Blood. ALMA HILLER and HERMAN O. MOSENTHAL (*J. Biol. Chem.*, 1916, **28**, 197—202).—In normal individuals, the blood contains about 78.5% of water. There may be a variation of about 1% of this concentration during the course of a few minutes

without any apparent cause. In those conditions, pathological or experimental, in which the amount of dextrose in the blood is diminished or increased, there is no corresponding change in the concentration of the water in the blood. In diabetes, for instance, the water content of the blood is normal, notwithstanding the hyperglycæmia and polyuria which may be present. H. W. B.

Changes in the Urea Content of Blood and Tissues of Guinea-pigs Maintained on an Exclusive Oat Diet. HOWARD B. LEWIS and WALTER G. KARR (*J. Biol. Chem.*, 1916, **28**, 17—25. Compare Funk, A., 1916, i, 696).—The appearance of scorbutic symptoms in guinea-pigs fed on an exclusive oat diet is accompanied by a large increase in the amount of urea in the blood and tissues. The addition of cabbage or orange juice to the diet prevents the disease, and simultaneously prevents the rise in the urea content of the blood and tissues of the animal. Sodium citrate cannot replace the cabbage or orange juice, so that the pathological condition cannot be due to the production of acidosis. A satisfactory explanation of the connexion between the scorbutic condition and the high urea figures is not given by the authors.

H. W. B.

Enzymes in Blood. G. SATTA (*Arch. ital. de Biol.*, 1915, **64**, 118—122; from *Physiol. Abstr.*, 1916, **1**, 296).—If the serum proteins are fractionated (the globulin being precipitated by carbon dioxide or salted out with sodium chloride), the following enzymes, tributyrase, amylase, and glycyl-*l*-tyrosinase, are contained in the albumin fraction.

G. B.

The Coagulation of the Blood. I. B. STUBER and R. HEIM (*Biochem. Zeitsch.*, 1916, **77**, 333—357).—Coagulation of plasma can be caused by the addition of glycerides, and the fatty acids have a specific action in causing this phenomenon. The coagulating action of the acid increases with increase in the number of carbon atoms in the acid, and acids such as palmitic and stearic acids exert therefore a greater coagulating action than the lower acids in the series. It is important, however, that an excess of acid is not added, as this inhibits the coagulation. The authors draw the conclusion that the optimal conditions for coagulation lie in the neighbourhood of the isoelectric point. The fats and fatty acids were added in the form of emulsions. It is conceivable that the coagulum is a complex of fibrin with a fatty acid, but this point is not definitely decided.

S. B. S.

The Coagulation of the Blood. II. B. STUBER and R. HEIM (*Biochem. Zeitsch.*, 1916, **77**, 358—374).—The action of ferments on the coagulation process was investigated, and it was found that those produce the greatest coagulative effect which possess the greatest lipoclastic activity, and there is a proportionality between this factor and the capacity for accelerating coagulation. The activity of the thrombokinas of Morawitz is due chiefly to the

substances contained therein which are soluble in ether, but the lipase of the liver is also a coagulating factor. The coagulative action of extracts of organs appears to be due to the fact that they contain fats and a lipase. S. B. S.

The Coagulation of the Blood. III. B. STUBER and FR. PARTSCH (*Biochem. Zeitsch.*, 1916, 77, 375—387).—The results of Bordet and Delange and of Zack are confirmed, according to which plasma which has been deprived of its lipid substances by extraction with ether and other organic solvents loses its capacity for coagulation. The fact is also confirmed that the coagulative power is restored by the addition of lipoids. This restorative action is not, as has been thought by other authors, a specific action of lecithin, but is the action of fats generally in the presence of a lipase. The results confirm the general conception of the authors as to the part played by fats and lipase in the coagulative process. S. B. S.

Fibrin and its Relationship to Problems of Biology and Colloidal Chemistry; the Problem of Blood Coagulation. X. The Micellar Crystalline Character of Fibrin. E. HEKMA (*Biochem. Zeitsch.*, 1916, 77, 273—282).—A general account is given of the conversion of the fibrin sols into gels and fibre, and the application of von Nægeli's micellar theory to these changes is discussed. S. B. S.

Structure of the Fibrin-gel and Theories of Gel-formation. W. H. HOWELL (*Amer. J. Physiol.*, 1916, 40, 526—553; from *Physiol. Abstr.*, 1916, 1, 223).—In the clotting of vertebrate blood, as observed under the ultramicroscope, the fibrin is first deposited as needles formed by an aggregation of fibrinogen particles. Vectorial forces, like those involved in crystallisation, are brought into play. The needles form a close meshwork and appear to become adherent. Under certain conditions, such as increased alkalinity, the gel may be devoid of this crystalline character and be formed by amorphous aggregation. The fibrin gel is clearly a heterogeneous system of a continuous, more liquid phase between trabeculae composed of crystalline needles and constituting the more solid phase. The structure is reticular or sponge-like, and not a honeycomb.

Fibrinogen may have either a positive or negative electrical charge, according to the reaction of the medium. The behaviour towards thrombin differs in the two cases, the vectorial characteristic being connected with the positive charge, or adsorption of hydrogen ions.

Since the gel has not a honeycomb structure, the retention of water and maintenance of shape, as if possessing solid properties, cannot be due to the merely mechanical enclosure of water in cells. It is suggested that the water is held at the surface of the solid phase by molecular forces, such as those responsible for adsorption.

G. B.

Metabolism of Dextrose in Surviving Organs. I. Action of Intestinal Tissue on Dextrose Circulating therein. U. LOMBROSO (*Atti R. Accad. Lincei*, 1916, [v], 25, ii, 390—395).—When Tyrode's solution containing dextrose is circulated in the intestinal segment of a dog, the proportion of dextrose in the circulating liquid undergoes marked diminution, which in some cases amounts to 50%. At the same time, the carbohydrate-content of the intestine shows an increase, but this is never more than sufficient to account for the disappearance of 30—35% of the dextrose. When defibrinated blood containing dextrose is similarly circulated, the diminution in the reducing power of the circulating liquid is even greater than when Tyrode's solution is used; in this case, the carbohydrate-content of the intestine also diminishes considerably, marked consumption of the pre-existent dextrose thus taking place.

Similar differences were observed with amino-acids circulating in surviving organs in solution in blood and in Ringer's solution, but in the present case the phenomenon is particularly marked, the volume of liquid traversing the intestine per unit of time being appreciably less when blood is used than with the artificial liquid. The results show, indeed, that the more closely the conditions of the artificial circulation approximate to those of the organ *in vivo*, the less is the quantity of dextrose accumulating in the intestine and the greater the tendency of the organ to destroy the dextrose circulating in it.

T. H. P.

Mechanism of the Diffusion of Electrolytes through the Membranes of Living Cells. IV. Ratio of the Concentration required for the Accelerating and Antagonistic Action on the Diffusion of Potassium Salts. JACQUES LOEB (*J. Biol. Chem.*, 1916, 28, 175—184. Compare this vol., i, 67).—The addition of a second salt to a $M/8$ -potassium chloride solution has the four following effects on *Fundulus* eggs according to the concentration: (1) Beginning with the lowest concentration of the second salt, the addition has often a slightly retarding effect on the diffusion of potassium chloride through the membrane into the egg; (2) with a further increase of the concentration of the second salt ($M/4$ -sodium chloride or $M/512$ -sodium citrate), an acceleration of the diffusion is noticeable (general salt effect); (3) with a still further increase of the concentration ($M/2$ - to M -sodium chloride or $M/256$ - to $M/128$ -sodium citrate), a retardation of the diffusion occurs (antagonistic salt effect); (4) with a still higher concentration the eggs are killed more rapidly, probably not through the diffusion of the potassium chloride, but of the second salt into the egg. The ratio of the antagonistic to the accelerating concentration was found to be about 2:1 for different sodium salts.

H. W. B.

Chinese Preserved Eggs. Pidan. KATHARINE BLUNT and CHI CHE WANG (*J. Biol. Chem.*, 1916, 28, 125—134).—Pidan is prepared by preserving ducks' eggs in a mixture of an infusion

of black tea, lime, salt, and wood ashes. After five months, the eggs are coated with rice hulls, and are then ready for eating.

The results of the analysis of pidan show that the following changes take place during its formation from fresh ducks' eggs: Water is transferred from the white to the yolk; alkali salts are absorbed from the preserving mixture; the lecithin and total ethereal extract diminish in quantity; and the ammonia nitrogen, amino-nitrogen, and total non-coagulable nitrogen increase very greatly. It is therefore evident that the production of pidan from fresh eggs is due to the combined action of alkali, bacteria, and enzymes on the proteins and phospho-lipoids in the eggs.

H. W. B.

Method for the Measurement of the Urea-excreting Function of the Kidneys. T. ADDIS and C. K. WATANABE (*J. Biol. Chem.*, 1916, **28**, 251—259).—The new method is based on the results of some experiments on rabbits. Urine and blood are collected simultaneously, and the ratio—urea in grams in one hour's urine to urea in grams in 100 c.c. of blood—determined before and after the ligature of one ureter, whilst the animals are taking similar food and the same amount of water. In most cases the ratio remains constant, because the single kidney remaining after the operation is sufficient to meet ordinary demands. If, however, urea is injected, additional strain is thrown on the kidneys, and the ratio after the operation is invariably lower than it is before the operation. The authors propose to employ the method for the early detection of pathological conditions arising from defective kidney function, such as Bright's disease.

H. W. B.

New Constituents of Milk. II. The Distribution of Phosphatides in Milk. THOMAS B. OSBORNE and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1916, **28**, 1—9. Compare A., 1915, i, 920).—By operating with very large quantities of milk, the authors are able to show that phosphatides can be extracted from the caseinogen precipitated by the addition of dilute hydrochloric acid to milk, as well as from the "lactalbunin" coagulum obtained by heating the filtrate from the caseinogen. The precipitate produced by treating skimmed milk, free from caseinogen and lactalbumin, with sodium hydroxide until neutral to phenolphthalein also contains a small amount of phosphatides, together with protein. The filtrate containing the non-protein constituents of milk contains at the most only minute traces of phosphatides.

A litre of milk contains about 27 milligrams of phosphatides which are intimately associated with the protein constituents of milk, and possibly combined with them as "lecithalbumins."

H. W. B.

Urinary and Fæcal Output of Calcium in Normal Men, together with Observations on the Hydrogen-Ion Concentration of Urine and Fæces. C. FERDINAND NELSON and J. L. WILLIAMS (*J. Biol. Chem.*, 1916, **28**, 231—236).—The authors have

measured the daily urinary and faecal output of calcium, calculated as oxide, over periods of 5 days for five apparently normal individuals of ages ranging from thirteen to seventy years. The urinary excretion varies from 0.1754 to 0.6186 gram, the faecal excretion from 0.4125 to 0.8010 gram, and the total daily excretion from 0.5879 to 1.4196 gram of calcium oxide. All the subjects studied were on ordinary mixed diets. The authors do not draw any conclusions regarding the relation between the observed hydrogen-ion concentration of the urine and the corresponding output of calcium.

H. W. B.

Calcium and Magnesium Content of Normal Urine. C. FERDINAND NELSON and W. E. BURNS (*J. Biol. Chem.*, 1916, **28**, 237—240).—The daily urinary output of calcium and magnesium has been estimated in the cases of twenty-five healthy individuals. In the majority of cases, the output of calcium exceeds that of magnesium. Apparently whichever element predominates does so constantly, or nearly so, and this phenomenon seems to be independent of the character of the food ingested.

H. W. B.

Influence of Sodium Carbonate, Administered by Duodenal Tube, on Human Diabetes. J. R. MURLIN and L. F. CRAVER, with WALTER L. NILES and WARREN COLEMAN (*J. Biol. Chem.*, 1916, **28**, 289—314).—Six cases of diabetes are described in which solutions of sodium carbonate or sodium hydrogen carbonate are introduced directly into the duodenum by means of an Einhorn's duodenal tube. In each case, the effects are a reduction of the glycosuria and hyperglycæmia. When the administration of alkali is discontinued, the dextrose in the blood and urine slowly returns to its original level.

H. W. B.

Pancreatic Diabetes in the Dog. IV. Influence of Pylorus Exclusion and of Gastrectomy on the Effects of Pancreatectomy. J. R. MURLIN and J. E. SWEET (*J. Biol. Chem.*, 1916, **28**, 261—288).—The authors believe that in pancreatic diabetes the hydrochloric acid produced in the stomach and left unneutralised in the duodenum is absorbed by the portal system and carried to the liver, where it exerts its toxic action (compare Murlin and Kramer, this vol., i, 69). If the acid is excluded from the duodenum by ligaturing the pylorus or by excision of the stomach, the onset of pancreatic diabetes after pancreatectomy should therefore be prevented or delayed. These operations have been carried out on dogs, and it is found that in most cases little or no glycosuria follows the subsequent operation of pancreatectomy. In the case of one dog, however, which was fed after gastrectomy on peptonised food introduced directly into the duodenum, so that a considerable amount of glycogen was probably stored in the liver previous to pancreatectomy, a severe diabetes with marked hyperglycæmia followed the removal of the pancreas. In general, dogs with the pancreas removed after gastrectomy do not exhibit the usual profound toxæmia of a simple pancreatectomy.

The authors suggest that the pancreatic hormone produced by the islands of Langerhans may be an alkaline substance which maintains the proper concentration of hydrogen ion in the tissues for the biochemical oxidation of dextrose. The internal secretion thus resembles the external secretion which contains the alkali requisite for the neutralisation of the hydrochloric acid entering the duodenum from the stomach.

H. W. B.

Composition, especially the Hydrogen-Ion Concentration, of Sea-water in Relation to Marine Organisms. J. F. McCLENDON (*J. Biol. Chem.*, 1916, 28, 135—152).—The P_H of sea-water at Tortugas, Florida, from the surface to a depth of 35 metres varies from 8.1 to 8.22, which is about the average usually found for ocean water.

An artificial sea-water in which even the most delicate marine organisms can be kept alive for considerable periods may be prepared from the following normal solutions: 22 c.c. of $M/2$ -calcium chloride, 50.21 c.c. of $M/2$ -magnesium chloride, 57.09 c.c. of $M/2$ -magnesium sulphate, 10.23 c.c. of M -potassium chloride, 488.65 c.c. of M -sodium chloride, 0.8 c.c. of M -sodium bromide, 2.32 c.c. of M -sodium hydrogen carbonate, and 373.63 c.c. of water. The mixture must be aerated until it has a P_H of about 8.15.

H. W. B.

A New Group of Antagonising Atoms. II. T. P. FEENSTRA (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, 19, 341—344).—In a previous paper (*ibid.*, 1916, 19, 99) it was shown that uranium can take the place of potassium in Locke-Ringer's solution, and that this substitution is not affected by the separation of the uranium from its products of transformation. Further experiments show that the potassium may also be replaced by thorium, but in this case it is not possible to say to what extent the action is due to radiothorium, since this cannot be separated from the thorium.

Both uranium and thorium are antagonistic to calcium in the same way as potassium and rubidium are, and the supposition that the antagonism is in some way connected with the valency of the ions does not appear to be consistent with the new observations.

H. M. D.

Elimination of Malates after Subcutaneous Injection of Sodium Malate. LOUIS ELSBERG WISE (*J. Biol. Chem.*, 1916, 28, 185—196).—Sodium malate may be injected subcutaneously into rabbits or cats in quantities up to 1 gram per kilo. without the occurrence of any toxic symptoms. Small amounts of the injected substance are recovered unchanged from the urine.

The method for the estimation of malic acid in urine described by Ohta (*A.*, 1912, ii, 1076) affords satisfactory results if the urine is saturated by the addition of powdered uranyl acetate instead of being treated with a saturated solution of the reagent.

H. W. B.

Action of Sodium Citrate and its Decomposition in the Body. WILLIAM SALANT and LOUIS E. WISE (*J. Biol. Chem.*, 1916, 28, 27—58).—The authors describe a method for the estimation of small amounts of citric acid in urine, based on Denigès's reaction. A modification of the method is employed for the approximate estimation of very small amounts of citrate in blood.

The ingestion of large quantities of sodium citrate by rabbits renders the urine alkaline. Only traces of citrate are found in these circumstances in the blood and urine, and toxic effects are not observed unless the amount of citrate ingested has been very large.

Sodium citrate disappears rapidly from the circulation after intravenous injection into rabbits, cats, and dogs; acute toxic symptoms are produced, the fatal dose varying from 0.4 to 1.6 grams per kilo. The urine remains free from citrate until the amount of citrate injected exceeds 0.5 gram per kilo.

The subcutaneous injection of sodium citrate may also occasion acute toxic symptoms.

H. W. B.

Tolerance to Morphine. II. The Specificity of the Tolerance. JOHANNES BIBERFELD (*Biochem. Zeitsch.*, 1916, 77, 283—297).—Dogs which have acquired tolerance to morphine by repeated injection of the drug do not acquire tolerance to scopolamine, cocaine, or even morphine derivatives, such as heroine (diacetylmorphine). The course of the acquisition to morphine is not influenced by feeding with cholesterol. After cessation for ten days of the injections, the cerebral reaction to morphine does not reappear, although the animal has not lost tolerance in some other respects. The immunising substances cannot always be detected when the serum of the immunised animals is transferred to other animals.

S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

General Conceptions of Intoxication. IV. The Nature of Substances which Accelerate the Formation of Ferments. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, 77, 402—404. Compare this vol., i, 71).—The substance in serum which promotes the capacity of bacteria for hydrolysing urea is soluble in water or alcohol, but insoluble in ether, light petroleum, or acetone.

S. B. S.

General Conceptions of Intoxication. V. The Stimulative Action of Dextrose on the Formation of Ferments. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, 77, 405—407).—Dextrose stimulates bacterial decomposition of urea.

S. B. S.

Biochemical Changes in Protein Cleavage Products produced by Bacteria. II. TAKAOKI SASAKI (*Acta Scholae Med., Kyoto*, 1916, 1, 103—113; from *Physiol. Abstr.*, 1916, 1, 283).—*Bacillus proteus*, freshly isolated from putrid pancreas, destroys tyrosine and converts it largely into *d*-hydroxyphenyl-lactic acid and, to a smaller extent, into hydroxyphenylpropionic acid. *Bacillus subtilis*, in pure culture from straw infusion, produces, on the other hand, the antipodal *l*-hydroxyphenyllactic acid, together with other substances as yet unidentified. G. B.

Influence of Short, Slight Rises in Temperature on the Progress of Fermentation. CHARLES RICHET and HENRY CARDOT (*Compt. rend.*, 1916, 163, 954—959).—If a liquid undergoing lactic fermentation is heated for five minutes at a temperature of 57—58°, the activity of the ferment is materially diminished. The effect is noticeable at the end of one minute, and increases considerably with the time. If the heating is repeated for further periods of five minutes, there is a further diminution in the acidity produced. Pathogenic organisms being much more susceptible to heat than the lactic ferment, the authors suggest the irrigation of wounds with water at 52—54° as a means of cleansing them.

W. G.

Action of Copper Sulphate on the Algæ of Potable Water. ATILIO A. BADO (*Pamphlet*, 1916, 15 pp.).—An account of the application of the copper sulphate method to the elimination of algæ from the water supply of Rio de la Plata. A. J. W.

Relationship existing between the Oxydase Activity of Plant Juices and their Hydrogen-Ion Concentrations. The Cause of Oxydase Activity in Plant Tissues. HERBERT H. BUNZELL (*J. Biol. Chem.*, 1916, 28, 315—333).—The results indicate that the greatest oxydase activity occurs at or near the neutral point, and that acids inhibit the action of oxydases. The author suggests that oxydase activity is due to the presence of colloidal proteins, which through surface action are capable of condensing oxygen as well as oxidisable substances at their surfaces, resulting in the oxidation of those substances. The differences in oxydase activity of the various plant tissues are therefore due to the differing composition of their respective proteins. H. W. B.

Occurrence and Physiological Significance of Flavone Derivatives in Plants. K. SHIBATA, I. NAGAI, and M. KISHIDA (*J. Biol. Chem.*, 1916, 28, 93—108).—The authors describe a new method for the detection of the presence of flavones in plant tissues. The tissue is extracted with hot alcohol, and a few c.c. of the extract are then heated with a drop of mercury the size of a pea, a small amount of magnesium powder, and a few drops of concentrated hydrochloric acid in a test-tube. In the presence of flavone derivatives, reduction takes place with a vigorous generation of hydrogen gas and the production of a red colour. The intensity of the colour produced is regarded as a measure of the amount of flavone present. By means of this test, the authors are

able to demonstrate the presence of flavone derivatives in almost all plants, including mosses, ferns, grasses, conifers, palms, and angiosperms.

The authors suggest that the flavone derivatives dissolved in the cell sap have to fulfil the important physiological function of absorbing the ultra-violet rays of the sunlight, by means of which the living protoplasm and its biochemical agencies are protected from the injurious action of the rays. In support of this theory, it is found that the flavone derivatives in plants are almost exclusively limited to the epidermis and the peripheral parenchymatous layer of the aerial parts. Further, plants growing in tropical or alpine regions are always rich in flavones, except those which are fully protected from the action of the excessive illumination by some means of a morphological or anatomical nature.

The green leaves of deciduous trees, which produce anthocyanin in autumn, contain a considerable quantity of flavone derivatives. The production of autumnal colour is due to the biochemical change resulting in the reduction of the already existing flavones in the leaf into anthocyanin.

H. W. B.

Kafirin, an Alcohol-soluble Protein from Kafir, *Andropogon sorghum*. CARL O. JOHNS and J. F. BREWSTER (*J. Biol. Chem.*, 1916, 28, 59—65).—The new protein, *kafirin*, constitutes more than one-half the total protein in kafir seeds. It contains C 55.19, H 7.36, O 20.41, N 16.44, and S 0.60%, and thus resembles zein. It differs from zein in containing lysine and tryptophan, and in requiring a larger proportion of 70% alcohol for its solution. The estimation of the diamino-acids by Van Slyke's method indicated the presence of 1.58% of arginine, 0.90% of lysine, and 1.0% of histidine in kafirin.

H. W. B.

Chemical Investigation of Rain Water Collected at Various Sites in the [Sheffield] City Area. W. PALMER WYNNE (Rep. to the Health Committee of the Sheffield City Council, 1914—15, 15 pp.).—A detailed account of the results obtained at Sheffield in connexion with the investigation of atmospheric pollution (*A.*, 1916, i, 592).

With reference to the method employed, it is pointed out that the greatest pollution occurs on calm, foggy days without rain, and that the monthly analyses of the rain-water fail to give any record of the atmospheric impurities under these conditions. The conclusion is drawn that the total amounts of impurities, as indicated by the sums of the monthly results, represent minimum values at most.

In the Attercliffe area, the results do not show the progressive increase in contamination which would be expected from the increased industrial activity.

It is suggested that more useful results could be obtained by drawing air through water, continuously and at a given rate, so as to retain all the impurities.

N. H. J. M.

Organic Chemistry

Relation between Filtration of the [Solid] Paraffins of Naphtha and their Adsorption. M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 718—720).—By a single filtration of naphtha through kaolin, the lower fraction of the solid paraffins is adsorbed to the same extent as by adsorption in other ways; the adsorption is irreversible, and hot water extracts nothing from the separated adsorbent. T. H. P.

Irreversible Adsorption of the "Carbonaceous Substances" of Petroleum. M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 720—724. Compare A., 1915, i, 489).—The adsorption of a 1% solution of petroleum in benzene by animal charcoal and by calcined kaolin has been investigated. The "carbonaceous substances," that is, those which cause polarimetric opacity, are adsorbed less rapidly by kaolin than by animal charcoal, but their adsorption is complete if the carbonisation constant (coefficient of polarimetric opacity) is not less than 18%. The adsorption is irreversible, neither boiling light petroleum nor boiling water extracting anything from the adsorbent after use. Other conclusions drawn from the results obtained are: (1) The qualitative and quantitative results of adsorption depend on the character and proportion of the adsorbent, but not on the mode of its application. (2) The velocity of adsorption is very high, since with a suitable concentration of the solution, filtration of the latter through a layer of adsorbent 2.5 cm. in thickness brings about adsorption. (3) The adsorbent used as filtering layer for petroleum may be regenerated by ignition.

The bearing of these results on the natural filtration-distillation processes of petroleum is discussed. T. H. P.

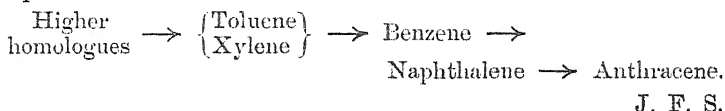
Pyrogenesis of Hydrocarbons. E. LAWSON LOMAX, A. E. DUNSTAN and F. B. THOLE (*J. Inst. Petrol. Tech.*, 1916, **3**, 36—120).—A general account of the subject is given, together with chronological lists of the literature and patents. T. H. P.

Thermal and Pressure Decomposition of Pentanes and Hexanes. G. EGLOFF (*Met. Chem. Eng.*, 1916, **15**, 692—696; from *J. Soc. Chem. Ind.*, 1917, **36**, 76).—The mixture of pentanes and hexanes used was derived from light petroleum after removal of unsaturated hydrocarbons; it had $D_{15.5}^{20} 0.656$, and, on distillation, yielded: b. p. below 40°, 36.0%; b. p. 40—60°, 29.0%; b. p. 60—70°, 34.2%. It was subjected to temperatures of 450°, 500°, 650°, and 725°, and pressures of 1 and 12 atmospheres, and the recovered oil examined for benzene, toluene, xylene, naphthalene, and anthracene. The percentage yield of recovered oil decreased with increase of pressure and temperature, the maximum yield

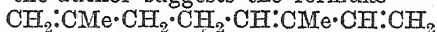
being obtained at 450° and 1 atmosphere. At 650° and 12 atmospheres, and at 725° and 1 atmosphere, the original oil decomposed completely into carbon and gas. The percentage of benzene in the recovered oil increased as pressure and temperature were increased, the maximum of 15.1% being found at 650° and 1 atmosphere. The toluene and xylene content of the recovered oil decreased with increased temperature and pressure, the maximum being 6.9% for toluene and 8.2% for xylene, both at 450° and 1 atmosphere. Naphthalene and anthracene in the recovered oil increased with temperature and pressure, a maximum of 5.6% for naphthalene and 4.2% for anthracene being obtained at 650° and 1 atmosphere. The yields of benzene, toluene, and xylene, calculated on the basis of the original oil, decreased with increase of temperature and pressure; the highest yields were 3.2% for benzene, 5% for toluene, and 5.9% for xylene, all at 450° and 12 atmospheres. Naphthalene and anthracene increased with increasing temperature and decreased with increasing pressure; the maximum for naphthalene was 1.7% and for anthracene 1.2%, both at 500° and 1 atmosphere. The mechanism of the formation of aromatic hydrocarbons from pentanes and hexanes is probably represented by the following scheme: pentanes and hexanes \rightarrow $C_5H_{10} + CH_4 \rightarrow C_2H_4 + C_3H_6 \rightarrow$ naphthenes \rightarrow aromatic hydrocarbons. H. W.

Effect of Temperature on the Formation of Benzene, Toluene, Xylene, Naphthalene, and Anthracene from Petroleum at Atmospheric Pressure. GUSTAV EGLÖFF and THOMAS J. TWOMEY (*J. Physical Chem.*, 1916, 20, 121-150).—A long historical review of the work done since the time of Faraday on the production of gas from various oils is given, and conclusions are drawn as to the relative amounts of the various constituents of the liquid products with variation of the conditions of the experiments. In the present series of experiments, weighed quantities of petroleum (574 grams) were passed through an electrically heated furnace at temperatures from 450° to 875°. The oil was fed into the furnace at a constant rate (246 grams per hour), and the amount of gas and liquid produced measured. The liquid was then distilled, and the fractions 170-230°, 230-270°, and 270° to tar collected. These were examined and their specific gravities recorded. The results of the experiments are given in numerous tables and curves. It is shown that the percentage of cracked oil obtained decreased slowly with increase of temperature from 450-550°; it decreased rapidly from 550° to 700°, and at a much slower rate from 700° to 875°. The formation of gas increased proportionally with change of temperature similarly to the percentage of the cracked oil. The density of the cracked oil increased with temperature. Temperatures of 450° to 600° produced in the cracked oil more toluene and xylene than benzene, and more toluene than xylene. No naphthalene or anthracene was formed at these temperatures. At 650° more toluene than benzene, and more benzene than xylene, were formed, but no naphthalene or

anthracene. Temperatures of 700° to 850° yielded uniformly more benzene than toluene or xylene, but more toluene than xylene. The formation of naphthalene began at 750°, and of anthracene at 800°, and both increased with the temperature. The formation of benzene in the cracked oil attained a maximum of 21% at 800°, of toluene 8·3% at 700°, and of xylene 7·2% at 700°. Beyond these respective temperatures, the formation of each decreased fairly rapidly with rise in temperature. The largest percentage of naphthalene obtained was 11·4 at 875°, and anthracene 2·5 at the same temperature. Temperatures 450° to 700° produced benzene, toluene, and xylene mixed with aliphatic compounds. The higher temperatures 750° to 875° yielded aromatic compounds practically free from aliphatic compounds. On the basis of the oil used, a maximum of 4·7% of benzene was obtained at 750°, 3·1% toluene at 650°, 1·9% xylene at 700°, 2·0% naphthalene at 800°, and 0·3% anthracene at 800°. The experimental evidence indicates that the formation of the individual aromatic compounds with change of temperature follows the scheme:



Refractometric Investigations of Hydrocarbons with Two and Three Conjugate Double Linkings at the Same Time. The Aliphatic Terpenes and their Derivatives. Synthesis of New $\alpha\gamma$ -Trienes. C. J. ENKLAAR (*Rec. trav. chim.*, 1917, 36, 215—246. Compare A., 1909, i, 111).—In the light of the behaviour of the ozonides of ocimene and *allo*-ocimene on decomposition, the author suggests the formulæ

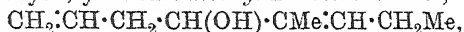


and $\text{CMe}_2\text{:CH}\cdot\text{CH}\text{:CH}\cdot\text{CH}\cdot\text{CMe}\text{:CHMe}$, respectively, for these hydrocarbons. In support of these views, he has determined the refractometric indices of a number of unsaturated hydrocarbons, two of which are new, and compared their values with those obtained for ocimene and *allo*-ocimene.

Tiglic aldehyde, D_4^{20} 0·8723; D_4^{25} 0·8764; n_D 1·44706, n_D 1·45117, n_D 1·46148, n_D 1·47080 at 9·6°; $E\Sigma$ Ref., 1·17; $E\Sigma$ Disp., 45%, when mixed in anhydrous ether with allyl bromide and the mixture slowly poured on to an excess of zinc, gave *ε*-methyl- $\Delta^{\alpha\gamma}$ -heptadien-8-ol, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}\text{:CHMe}$, b. p. 172—173°/760 mm., D_4^{20} 0·8766, n_D 1·46174, n_D 1·46481, n_D 1·47278, n_D 1·47945 at 11·8°. This alcohol, when heated with potassium hydrogen sulphate (compare A., 1913, i, 243), gave a liquid which, when distilled over sodium, yielded three fractions, b. p. 78—82°/96 mm., 82—83·5°/96 mm., and 83·5—85°/96 mm. This liquid is *ε*-methyl- $\Delta^{\alpha\gamma}$ -heptatriene, the physical constants for the three fractions being: (1) D_4^{20} 0·7891, n_D 1·51798, n_D 1·52595, n_D 1·54806, n_D 1·56939 at 14·7°; (2) D_4^{20} 0·7938, n_D 1·52475, n_D 1·53301, n_D 1·55618, n_D 1·57854 at 15·3°; (3) D_4^{20} 0·7965, n_D 1·52620,

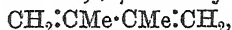
n_D 1.53466, n_B 1.55811, n_γ 1.58114 at 15°. This hydrocarbon readily polymerises, either during distillation or in the presence of acids. Attempts at hydrogenation by means of sodium in absolute alcohol only yielded resins and a very small amount of a liquid, b. p. 133—135°. At -20° it readily absorbs two atoms of bromine, and the bromide formed slowly absorbs two more atoms of bromine. It readily absorbs oxygen and gives an isonitroso-compound.

$\alpha\beta$ -Methylethylacraldehyde, when treated in the same way as the tiglic aldehyde, yielded ϵ -methyl- $\Delta^{\alpha\gamma}$ -octadien-6-ol,



b. p. 85.5—87°/18 mm., D_4^{20} 0.8644, n_a 1.45867, n_D 1.46177, n_B 1.46963, n_γ 1.47617 at 17.2°. This alcohol, when dehydrated with potassium hydrogen sulphate, gave ϵ -methyl- $\Delta^{\alpha\gamma}$ -octatriene, obtained in three fractions, b. p. 85°/36 mm., 85—87°/36 mm., 87°/36 mm. Of these, the first and third fractions had the physical constants: (1) n_a 1.50873, n_D 1.51584, n_B 1.53568, n_γ 1.55452 at 23°; (3) n_a 1.52465, n_D 1.53349, n_B 1.55632 at 23.2°.

The specific and molecular refractions for the various lines of the principal and higher boiling-point fractions of *allo*-ocimene have been recalculated in the light of more recent work, and are tabulated. These are compared in the light of the rules of Auwers and Eisenlohr (compare A., 1911, ii, 781) against the values for certain methylbutadienes. $\Delta^{\beta\gamma}$ -Hexadiene, $\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHMe}$, b. p. 77—78°, D_4^{25} 0.7273, n_a 1.45133, n_D 1.45591, n_B 1.46800, n_γ 1.47855 at 12.5°; δ -methyl- $\Delta^{\alpha\gamma}$ -pentadiene, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$, b. p. 73.9—74.8°/750 mm., D_4^{16} 0.7229, n_a 1.44125, n_D 1.44580, n_B 1.45720, n_γ 1.46755 at 13°; isoprene, $\text{CH}_2\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2$, b. p. 33.8—34.3°/756 mm., D_4^{18} 0.6849, n_a 1.41818, n_D 1.42245, n_B 1.43371, n_γ 1.44367 at 13°; $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene,



D_4^{16} 0.7304, n_a 1.43486, n_D 1.43866, n_B 1.44972, n_γ 1.45832 at 13°.

These, when converted into molecular refractions and compared with the values for ocimene recalculated by using Eisenlohr's atomic constants (compare A., 1911, ii, 81), indicate that in ocimene there is a system of double linkings interrupted once in

	$E_{\Sigma a.}$	$E_{\Sigma b.}$	$E_{\Sigma \beta - a.}$	$E_{\Sigma \gamma - a.}$
$\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHMe}$	1.96	2.03	52%	53%
$\text{CMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$	1.36	1.44	43	49
$\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2$	1.14	1.20	39	45
$\text{CH}_2\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CH}_2$	0.54	0.56	33	34
Ocimene	1.17	1.24	41	47

the centre by a side-chain, this being opposed to Eisenlohr's views (*loc. cit.*).

The decane which is obtained by the hydrogenation of ocimene with active nickel has b. p. 160—161°/760 mm., D_4^{20} 0.7289, n_a 1.40891, n_D 1.41103, n_B 1.41603, n_γ 1.42024 at 20.2°, these values being in agreement with those for the decane obtained from geraniol.

In a supplement to the paper, the author describes a modifica-

tion of the method of filling the tube for a lead chromate combustion for use in the analysis of volatile substances, which are difficult to burn, with which it is possible to obtain accurate results.
W. G.

The Melting Points of some Hydrocarbons, in particular of Dienes, having a System of Conjugate Double Linkings. C. J. ENKLAAR (*Rec. trav. chim.*, 1917, 36, 247—249).—In an endeavour to find some relationship between the melting points of unsaturated hydrocarbons with conjugate double linkings and the corresponding saturated hydrocarbons, the author has tried to determine the melting points of nine such hydrocarbons, and finds that although these hydrocarbons, except dihydromyrcene and $\beta\zeta$ -dimethyloctane, become solid and crystalline at low temperatures, they do not melt sharply, the process being spread over a rather wide range of temperature in each case. W. G.

Union of Hydrogen with Acetylenic Derivatives. Hydrogenation of Dimethyldiethylbutinenediol [$\gamma\zeta$ -Dimethyl- Δ^8 -octinene- $\gamma\zeta$ -diol]. Y. S. ZALKIND and (MILE.) V. MARKARJAN (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 538—550. Compare A., 1915, i, 640).—In presence of colloidal palladium, $\beta\epsilon$ -dimethyl- Δ^7 -hexinene- $\beta\epsilon$ -diol (compare A., 1914, ii, 257; 1915, ii, 435) or $\gamma\zeta$ -diethyl- Δ^8 -octinene- $\gamma\zeta$ -diol combines with two atoms of hydrogen, hydrogenation proceeding only very slowly after the formation of the ethylenic glycol. In the former case, however, the hydrogenation is quite rapid, and the velocity of the reaction is approximately proportional to the relative amount of catalyst employed. Hydrogenation of the second of the two above acetylenic glycols is much slower, and the velocity soon reaches a maximum value when the amount of catalyst is increased; thus, identical results are obtained with 0.01, 0.02, or 0.03 gram of colloidal palladium per 0.01 gram-mol. of the glycol in 30 c.c. of alcohol.

On account of these differences, the authors have now investigated the hydrogenation of $\gamma\zeta$ -dimethyl- Δ^8 -octinene- $\gamma\zeta$ -diol, which occupies an intermediate position to the above two acetylenic glycols; this glycol has m. p. 54—55° (compare Dupont, A., 1914, i, 134), and not 48—49° as stated by Iocitsch (A., 1914, i, 403). Here also, in presence of colloidal palladium, two atoms of hydrogen are added, and the velocity and the manner of its variation with the quantity of palladium are intermediate to those observed in the two cases referred to above.

In ethereal solution containing platinum black, the acetylenic glycol unites with four atoms of hydrogen, and there is no break in the hydrogenation at the point corresponding with the addition of two atoms. The magnitude of k remains constant until 85—90% $2H_2$ are absorbed, and subsequently increases markedly in consequence of further hydrogenation of the saturated glycol; Dupont (*loc. cit.*), indeed, obtained $\gamma\zeta$ -dimethyloctan- γ -ol in this case.

$\gamma\zeta$ -Dimethyl- Δ^8 -octene- $\gamma\zeta$ -diol, $\text{OH}\cdot\text{CMeEt}\cdot\text{CH}\cdot\text{CH}\cdot\text{CMeEt}\cdot\text{OH}$, obtained by hydrogenation of $\gamma\zeta$ -dimethyl- Δ^8 -octinene- $\gamma\zeta$ -diol in presence of colloidal palladium, is a viscous, odourless, colourless liquid, D_4^{20} 0.9349, D_4^{25} 0.9216, n_D^{20} 1.45593, which does not distil unchanged, even in a vacuum. When it is acetylated, one of the hydroxyl groups is lost as water, with formation of a double linking, whilst the other undergoes normal acetylation; the *product*, $\text{C}_{12}\text{H}_{20}\text{O}_2$, b. p. 170—190°, or 100—140°/38 mm., thus represents the acetyl derivative of a diethylenic alcohol. When distilled in a vacuum, $\gamma\zeta$ -dimethyl- Δ^8 -octene- $\gamma\zeta$ -diol loses the elements of water, yielding the corresponding *oxide*, $\text{C}_{10}\text{H}_{18}\text{O}$, which was obtained pure by dehydration of the ethylene glycol with sulphuric acid, and is a mobile liquid with an odour like that of camphor, b. p. 156—158°, D_4^{20} 0.8592, D_4^{25} 0.8480, n_D^{25} 1.43508.

$\gamma\zeta$ -Dimethyloctane- $\gamma\zeta$ -diol, $\text{OH}\cdot\text{CMeEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{OH}$, obtained by hydrogenation in presence of platinum black, is a viscous, odourless, colourless liquid, D_4^{20} 0.9363, D_4^{25} 0.9255, n_D^{20} 1.45523. This glycol also loses the elements of water on acetylation, one hydroxyl group alone undergoing acetylation; the resulting *acetylated ethylenic alcohol*, $\text{C}_{12}\text{H}_{22}\text{O}_2$, is a liquid, b. p. 110—140°/37 mm., with a pleasant odour, and decolorises bromine and alkaline permanganate. When $\gamma\zeta$ -dimethyloctane- $\gamma\zeta$ -diol is distilled in a vacuum, it loses $1\text{H}_2\text{O}$, the principal product being an *unsaturated alcohol*, $\text{C}_{10}\text{H}_{20}\text{O}$, b. p. 162—165°, D_4^{20} 0.8364, D_4^{25} 0.8260, n_D^{25} 1.42997, which rapidly decolorises bromine water and alkaline permanganate solution; a small proportion of the γ -oxide is also formed.

T. H. P.

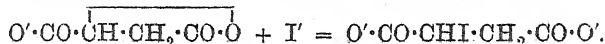
Stability of Mercuric Lactate and its Aqueous Solutions.
Preparation of Mercuric Lactate. MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1917, [vii], 15, 33—41).—Dry mercuric lactate may be kept for an indefinite period without undergoing decomposition, but its aqueous solution, particularly when concentrated, is less stable, the mercuric lactate changing gradually to mercurous lactate. A 0.1% solution remains almost unaltered for about three months, only 1.25% of the salt being reduced during this time, but if mercuric oxide is present, the rate of the reduction is accelerated considerably. To prepare mercuric lactate, a mixture of 100 grams of lactic acid and 400 grams of water is boiled until the residual solution weighs 320 grams (this operation decomposes any anhydride which may be present), the solution is then cooled, and 105 grams of yellow mercuric oxide are added in small quantities at a time. After one hour, the mixture is filtered, the filtrate is poured into shallow dishes, and seeded with a crystal of the salt. The crystals formed are separated, washed with small quantities of water, and dried at the ordinary temperature. Mercurous lactate may be prepared by heating 400 grams of water, 100 grams of lactic acid, and 100 grams of mercuric oxide on a water-bath for one hour, then filtering the mixture, and heating the filtrate for some hours; the mercurous lactate separates gradually as a precipitate.

W. P. S.

Stereochemical Studies. II. Action of Potassium Xanthate on Salts of the Halogeno-succinic Acids. BROR HOLMBERG (*Arkiv Kem. Min. Geol.*, 1916, 6, No. 8, 1—56).—Further measurements on the velocity of lactone-formation from *l*-bromosuccinic acid (compare Johansson, A., 1912, ii, 544, and Holmberg, A., 1914, i, 139) have been carried out, both with the pure potassium salt alone and in the presence of potassium nitrate. Consideration of all the results hitherto obtained shows that the velocity of lactone-formation increases only very slightly with increase in concentration of the metal ion present. There is no evidence that "cation catalysis" takes place to any considerable extent. The *l*-bromosuccinic acid used had $[\alpha]_D^{17} - 76.5^\circ$.

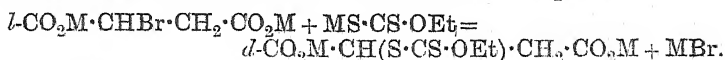
Similar results were obtained with the potassium and strontium salts of *l*-chlorosuccinic acid; the acid had $[\alpha]_D^{16} - 55.7^\circ$. The velocity of lactone-formation is much smaller than with the bromo-acid.

Pure *l*-iodosuccinic acid was prepared by the action of potassium iodide on *d*-lactonemalic acid, and had $[\alpha]_D^{15} - 81.3^\circ$. For experiments on the velocity of lactone-formation, the inactive acid, prepared from *l*-bromosuccinic acid and sodium iodide in acetone solution, was used. Exact determinations could not be carried out, but the results indicated that the velocity is greater than with the bromo-acid. Retardation, however, takes place to a considerable extent, owing to the iodide formed, since the reaction

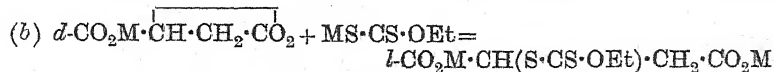
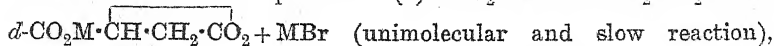


is reversible.

Velocity measurements on the action of potassium xanthate on salts of bromosuccinic acid showed that xanthosuccinic acid is formed in two ways, namely: (1) By direct substitution of bromine by the xanthate residue, in accordance with the equation



This reaction is bimolecular, and takes place slowly. (2) By addition of xanthate to the primarily formed lactonemalic acid salt, in accordance with the equations: (a) $l\text{-CO}_2\text{M} \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{M} \rightleftharpoons$



(very quick reaction). The reaction (1) is accelerated by metal ions to a much greater extent than (2a). The chloro- and iodo-succinic acids gave similar results, but with the former acid direct substitution played a lesser, and with the latter acid a greater, part than in the case of the bromo-acid. In the case of iodosuccinic acid, even in dilute solutions, the iodide formed during the reaction retarded the formation of xanthosuccinic acid from the lactonemalic acid, with the result that the total velocity of the

reaction between potassium xanthate and the iodosuccinates was less than when the bromosuccinates were used.

The results of the kinetic experiments necessitated a revision and extension of the author's previously published results (compare A., 1914, i, 139) on the reaction between potassium xanthate and lactonemalic acid. It is shown that the xanthate adds on to the lactonemalic acid, both in weakly acid and weakly alkaline solutions, giving a lævoxanthosuccinic acid with practically the maximum rotation. In slightly acid solution, the reaction is practically quantitative, but the yield is diminished in strongly acid solution, owing to the precipitation and decomposition of the xanthic acid; in alkaline solution, the yield is also diminished by saponification of the lactonemalic acid.

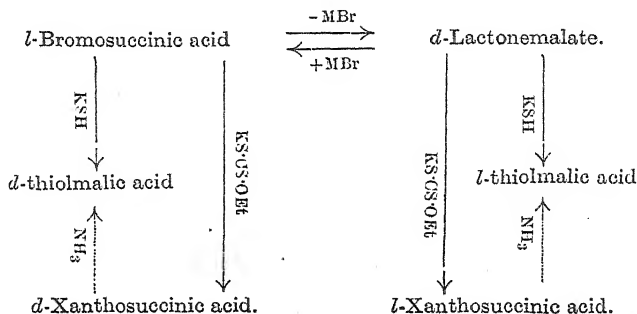
Since the addition of xanthate to the primarily formed lactonemalic acid gives *l*-xanthosuccinic acid, the formation of the *d*-acid must be ascribed to direct substitution in accordance with equation (1). It does not therefore seem any longer necessary to ascribe a special stereochemical action to "cation catalysis," all the changes which take place being explicable by the equations given above. It follows that all the factors which favour reaction (1) or retard reaction (2a) will make the product richer in dextro-acid or poorer in lævo-acid, and vice versa. The correctness of these conclusions is shown by reference to the author's previous paper (*loc. cit.*), and also, for example, by the following experiments, which show how necessary it is to work under well-defined conditions when investigating the Walden transformation. In a given experiment, the reaction (1) will be most in evidence at the beginning, since the concentrations of the reacting substances are then the greatest. It follows that the xanthosuccinic acid formed at the commencement of the reaction will be more strongly dextrorotatory than that formed later. This was shown to be the case when strontium *l*-bromosuccinate was used; the strontium xanthosuccinate is only sparingly soluble, and the first portions which separated out gave a dextrorotatory acid. The next fraction gave an acid which was less dextrorotatory, and the succeeding fractions gave acids which were more and more lævorotatory. Similar results were obtained with *l*-chloro- and *l*-iodo-succinic acids. Owing to the variation in the relative velocities of the reactions (1) and (2a) with these acids, it was found, for example, that at concentrations where the *l*-iodosuccinic acid gave *d*-xanthosuccinic acid, the *l*-bromo-acid gave a weakly, and the *l*-chloro-acid a strongly lævorotatory xantho-acid.

Temperature was found to have a very great influence on the reaction. Thus a solution which was 0.65 molar with respect to potassium *l*-bromosuccinate and potassium xanthate gave, at 0°, a xanthosuccinic acid with $[\alpha]_D + 30.6^\circ$; at 11–12° the xantho-acid formed had $[\alpha]_D + 8.3^\circ$, at 25° the product had $[\alpha]_D - 13.8^\circ$, and at 40° $[\alpha]_D - 40.1^\circ$. These big differences in the rotation of the product do not indicate that the temperature quotients of the reactions (1) and (2a) are very different, since calculation shows that if the velocity constant of the reaction (1) is doubled by a rise in

temperature from 15° to 25°, that of the reaction (2a) is thereby trebled.

Comparison of the above results with those obtained in the reaction between potassium hydrogen sulphide and potassium *l*-bromosuccinate (A., 1916, i, 307) shows that the substitution of bromine by the $\cdot\text{SH}$ residue takes place quicker than the substitution by the xanthate residue. Also, since the reaction (2a) is the same in both cases, the total velocity of reaction should be greater with potassium hydrogen sulphide than with potassium xanthate; this was confirmed experimentally.

Since the active xanthosuccinic acids when acted on by ammonia give thiolmalic acids with the same sign of rotation, all the results hitherto obtained can be expressed by the following scheme:



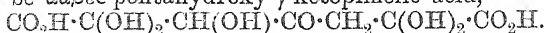
Since in the decomposition by ammonia reaction does not take place at the asymmetric carbon atom, no change in configuration will take place when the xanthosuccinic acids are transformed into the thiolmalic acids. From the other reactions one can reasonably conclude that potassium bromide, hydrogen sulphide, and xanthate behave stereochemically in the same way towards lactonemalic acid, and therefore that *l*-bromosuccinic acid has the same configuration as *l*-mercapto- and *l*-xantho-succinic acids. It follows that *stereochemical transformation takes place in the direct substitution of bromine in bromosuccinic acid by the $\cdot\text{SH}$ residue or the xanthate residue*, that is, in the bimolecular reaction (1). Similarly with the *l*-chloro- and *l*-iodosuccinic acids.

T. S. P.

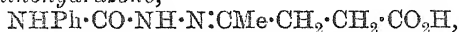
Constitution of Meconic Acid. W. BORSCHÉ (*Ber.*, 1916, 49, 2538—2546).—Meconic acid is usually regarded as the trihydrate of a derivative of 4-pyrone, $\text{C}_7\text{H}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$. This being so, it should yield various derivatives of pentamethylene oxide on reduction with hydrogen in the presence of colloidal palladium (compare other 4-pyrones, A., 1915, i, 574), but instead of this it gives $\alpha\beta\gamma\epsilon$ -tetrahydroxypimelic acid. It would appear, therefore, that in this case the pyrone ring is ruptured during reduction, but the nearly related, undoubted 4-pyrones, comenic acid, and pyromeconic acid, give normal pentamethylene oxide products, from which it follows

f*

that meconic acid is most probably not a pyrone at all. It is presumed to be $\alpha\alpha\beta\epsilon\epsilon$ -pentahydroxy- γ -ketopimelic acid,



$\alpha\beta\gamma\epsilon$ -Tetrahydroxypimelic acid crystallises in white granules, m. p. 210—215° (decomp.), and forms a *disilver* salt. When heated with concentrated hydrochloric acid in a sealed tube at 125—145° it yields lævulic acid, which may be identified by conversion into the *phenylcarbamino*hydrazone,



stout, white needles, m. p. 185—186° (decomp.), by mixing the neutralised product with phenylcarbamio hydrazide hydrochloride. The dry acid also yields the *diacetate* of a *pimelodilactone*, $\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{CH}\cdot\text{O}\cdot\text{CO}$

$\text{CO}\text{---O---CH---CH}\cdot\text{OAc}$, when heated with acetic anhydride and sulphuric acid, as prismatic tablets, m. p. 169—170°. The acid does not reduce Fehling's solution or ammoniacal silver oxide, but the mother liquor from the first reduction product contains a small amount of a powerfully reducing acid, which is probably α -hydroxy- $\gamma\delta$ -diketohexioic acid, as it forms a *disemicarbazone*, $\text{C}_8\text{H}_{14}\text{O}_5\text{N}_6$, m. p. 220° (decomp.).

Comenic acid, reduced under the same conditions, yields *hexahydrocomenic acid* ($\gamma\delta$ -dihydroxypentamethylene-oxide- α -carboxylic acid), $\text{C}_6\text{H}_{10}\text{O}_5$, which crystallises in hard needles, m. p. 172°, and forms a saturated *lactone*, $\text{C}_6\text{H}_8\text{O}_4$, b. p. 205°/18 mm., on heating.

Pyromeconic acid gives a mixture of a small amount of a tetrahydro- with much of a hexahydro-derivative. The latter may be separated in the form of its *diacetate*, $\beta\gamma$ -*diacetoxypentamethylene-oxide*, $\text{C}_9\text{H}_{14}\text{O}_5$, a fairly mobile liquid, b. p. 138—140°/18 mm., whilst the former, β -hydroxy- γ -ketopentamethylene oxide, becomes oxidised to the diketone when its aqueous solution is heated in the air, and this may be characterised as a *di-phenylcarbamino*hydr-

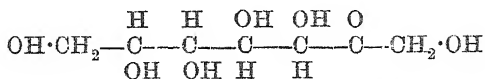
azone, $\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$
 $\text{O---CH}_2\text{---C}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, m. p. 215—216° (decomp.).

J. C. W.

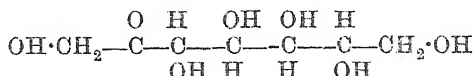
d-Mannoketoheptose, a New Sugar from the Avocado.

F. B. LA FORGE (*J. Biol. Chem.*, 1917, **28**, 511—522).—The new sugar is obtained by aqueous extraction of the avocado pear, *Persea gratissima*. *d*-Mannoketoheptose, $\text{C}_7\text{H}_{14}\text{O}_7$, crystallises in six-sided prisms, m. p. 152°, $[\alpha]_D^{20} + 29\cdot17^\circ$. It is not fermented by yeast, and does not show mutarotation. It gives a colour reaction with orcinol and hydrochloric acid like other heptoses and the pentoses. The *p*-bromophenylhydrazone, $\text{C}_{13}\text{H}_{19}\text{O}_6\text{N}_2\text{Br}$, crystallises in thin plates which are usually slightly yellow, m. p. 179°. On treatment with benzaldehyde the sugar is regenerated. The phenylosazone is identical with the osazone prepared from *d*-mannoaldohexose. On reduction with sodium amalgam, *d*-mannoketoheptose forms *d*-perisitol (compare Bertrand, A., 1909, i, 634) and *d*- β -mannoheptitol. These considerations indicate that the new sugar must be a mannoheptose, for which three structural formulæ are possible. It is possible to differentiate between them by means of the *p*-bromo-

phenylhydrazone derivatives. *d*- α -Mannoaldoheptose - *p*-bromophenylhydrazone, $C_{13}H_{19}O_6N_2Br$, has m. p. 207—208°, whilst the corresponding β -derivative is uncrystallisable. The new sugar must therefore be the *d*-mannoketoheptose represented by the configuration:



Perseulose (Bertrand, A., 1908, i, 715) is shown to be *l*-galactose, with the structural formula:



The pulp of the avocado also contains a gum which on hydrolysis yields *l*-arabinose. H. W. B.

Crystallographic and Optic Properties of Mannoketoheptose and of the Osazones of Mannoketoheptose and Mannoaldoheptose. F. E. WRIGHT (*J. Biol. Chem.*, 1917, 28, 523—526. Compare La Forge, preceding abstract).—For details the original paper must be consulted. The osazones of mannoketoheptose and mannoaldoheptose are identical. H. W. B.

Purification of Vegetable Fibres. G. L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 301—302).—The purification of vegetable fibres (cotton, flax) to be used in the study of adsorption in general, and that of colouring matters in particular, may be effected as follows. The fibre is boiled with water, which is changed each day after boiling for eight hours, this procedure being followed until 250 c.c. of the filtered water after use leaves no residue on evaporation. The extracted fibre is left for three days covered with alcohol, which is then replaced by a fresh quantity. After another period of three days, the fibre is removed from the alcohol and washed with ether, alcohol, and water successively. The complete displacement of the alcohol by water is effected only very slowly at the ordinary temperature, since even after eight months a fresh quantity of water was found to contain alcohol after being in contact with the fibre for a few days. The process takes place far more rapidly when the fibre is boiled with successive quantities of water. T. H. P.

Synthesis of Polypeptides, in the Construction of which the Amino-acids Glycine, Alanine, Leucine, and Cystine take Part. EMIL ABDERHALDEN and ERNST WYBERT (*Ber.*, 1916, 49, 2449—2473, 2838).—The synthesis of polypeptides containing residues of the amino-acids which have striking qualitative reactions appears to be worthy of attention for at least two reasons. In the first place, a knowledge of their properties would be a valuable guide in the development of methods for the separation and isolation.

tion of the polypeptides obtained by the hydrolysis of proteins, and in the second they would be useful material for studies on enzymes. A number of cystine derivatives are now described, some of them having been obtained previously by E. Fischer, and their important properties are tabulated.

For comparison with dichloroacetyl-L-cystine (Fischer and Suzuki, A., 1905, i, 30), the authors have made by the same process dibromoacetyl-L-cystine, $[\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2]_2\text{S}_2$, decomp. 160° , $[\alpha]_D^{20} - 107.97^\circ$ (alcohol), and di-iodoacetyl-L-cystine, needles, decomp. 150° , $[\alpha]_D^{20} - 95.35^\circ$. The diglycylcystine (*ibid.*) obtained from these by the action of ammonia reacts with D- α -bromoisohexoyl chloride to form di-D- α -bromoisohexoyldiglycyl-L-cystine, m. p. 147° (decomp.), $[\alpha]_D^{20} - 21.76^\circ$, and this yields di-L-leucyldiglycyl-L-cystine, when left with ammonia, as an amorphous powder, decomp. $190\text{--}213^\circ$, $[\alpha]_D^{20} - 72.24^\circ$ (in water), -75.45° (in N-HCl), which gives a very definite biuret reaction, and is precipitated from its aqueous solution by salt or ammonium sulphate.

Di-L- α -bromopropionyl-L-cystine, m. p. 141° , $[\alpha]_D^{20} - 133.23^\circ$, is prepared from L- α -bromopropionyl chloride and cystine and converted into di-L-alanyl-L-cystine, H_2O , scales, decomp. above 203° , $[\alpha]_D^{20} - 227.90^\circ$. The corresponding di-D- α -bromopropionyl-L-cystine crystallises in bundles of feathery needles, m. p. 142° , $[\alpha]_D^{20} - 96.96^\circ$, and the di-D-alanyl-L-cystine separates with H_2O , $[\alpha]_D^{20} - 137.40^\circ$ (in N-HCl). The latter differs from the L-alanyl and DL-alanyl compounds (*ibid.*) in being almost insoluble in alcohol. It reacts with D- α -bromoisohexoyl chloride to form di-D- α -bromoisohexoyldi-D-alanyl-L-cystine, decomp. 160° , $[\alpha]_D^{20} - 52.67^\circ$, and this yields di-L-leucyldi-D-alanyl-L-cystine, decomp. 203° , $[\alpha]_D^{20} - 115.29^\circ$ (water), -126.77° (N-HCl), in the usual way. This pentapeptide gives a very strong biuret reaction.

Di-L-leucyl-L-cystine (Fischer and Gerngross, A., 1909, i, 367) reacts with chloro- and bromo-acetyl chlorides to form dichloroacetyldi-L-leucyl-L-cystine, decomp. 120° , $[\alpha]_D^{20} - 102.8^\circ$, and dibromoacetyldi-L-leucyl-L-cystine, decomp. $120\text{--}166^\circ$, $[\alpha]_D^{20} - 55.81^\circ$, and the latter may be converted into diglycyldi-L-leucyl-L-cystine, $[\alpha]_D^{20} - 108.86^\circ$ (water), -134.46° (N-HCl), which also gives the biuret reaction.

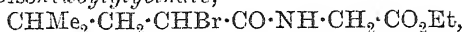
A further problem in connexion with the polypeptides obtained from proteins is the order in which the amino-acid residues occur. If it is possible to fix the free amino-groups by some acid residue which is not readily removed on hydrolysis, then it might be possible to say to which amino-acids in the peptide these free groups belong. Naphthalenesulphonyl residues are promising in this respect. If di- β -naphthalenesulphonyldiglycyl-L-cystine (Fischer and Bergell, 1902—1903) is boiled with 10% hydrochloric acid, it is hydrolysed to cystine and β -naphthalenesulphonylglycine, showing that the amino-groups of glycine are the free ones in diglycylcystine.

When the amino-acid ester mixture obtained from proteins is distilled, decomposition products containing sulphur and ammonia are formed at higher temperatures. This is largely, and perhaps exclusively, due to the cystine esters, for it is found that these

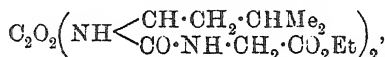
decompose in this way at above 120° in a high vacuum. *Cystine diethyl ester dihydrochloride* crystallises in bundles of silky needles.

J. C. W.

The Action of Oxalyl Chloride on some Amino-compounds. J. TH. BORNWATER (*Rec. trav. chim.*, 1917, **36**, 250—257).—A continuation of previous work (compare A., 1911, i, 617; 1916, i, 20). When ethyl sarcosinate hydrochloride is boiled in dry benzene with oxalyl chloride, *ethyl oxalyldisarcosinate*, $C_3O_2(NMe \cdot CH_2 \cdot CO_2Et)_2$, m. p. 76° , is obtained. α -Bromoisohexoyl chloride condenses with ethyl glycinate in dry benzene, giving *ethyl α -bromoisohexoylglycinate*,



white needles, m. p. 88° , which does not condense with oxalyl chloride in boiling benzene solution. Ethyl leucylglycinate gives, with oxalyl chloride, *ethyl oxalyldileucylglycinate*,



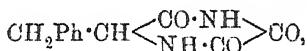
m. p. 151° .

Ethyl fumaryldiglycinate (compare Fischer and Koenigs, A., 1905, i, 31) when shaken with a 25% aqueous solution of ammonia gives *fumaryldiglycinamide*,



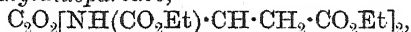
thin, glistening plates, m. p. 260° (decomp.). This amide does not react with oxalyl chloride in benzene solution, probably owing to its insolubility in benzene.

Ethyl phenylalaninate hydrochloride with oxalyl chloride yields *ethyl oxalyldiphenylalaninate*, $C_2O_2[NH(CO_2Et) \cdot CH \cdot CH_2Ph]_2$, m. p. 123.5° . When ethyl phenylalaninate hydrochloride is shaken with 25% ammonium hydroxide solution it yields *phenylalaninamide*, $CH_2Ph \cdot CH(NH_2) \cdot CO \cdot NH_2$, m. p. 138 — 139° , which with oxalyl chloride gives 2:3:6-triketo-5-benzylpiperazine,



m. p. 170° .

Ethyl aspartate hydrochloride condenses with oxalyl chloride, giving *ethyl oxalyldiaspartate*,



white needles, m. p. 108.5° .

W. G.

Preparation of Guanidine. J. SMITH SHARPE (*J. Biol. Chem.*, 1917, **28**, 399—401).—Guanidine thiocyanate is formed by heating dry ammonium thiocyanate for twenty hours at a temperature from 190° to 200° . The resulting mass is extracted with water and treated with potassium carbonate, which transforms the guanidine thiocyanate into guanidine carbonate and potassium thiocyanate. After drying, the latter substance is removed by 90% alcohol and the residual guanidine carbonate recrystallised from dilute alcohol. The yield is 15—20% of the ammonium thiocyanate employed.

H. W. B.

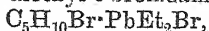
Lead Diethyl Compounds. SVEND MÖLLER and PAUL PFEIFFER (*Ber.*, 1916, **49**, 2441—2444).—Some of the lead diethyl compounds recently described by Grüttner and Krause (*A.*, 1916, i, 799, 800) had also been obtained independently, by another method, by the present workers. They convert lead tetraphenyl (*A.*, 1904, i, 544) into lead diphenyl dibromide by the action of bromine, treat this with magnesium ethyl bromide, and so obtain *lead diphenyl-diethyl*, PbEt_2Ph_2 , a colourless, highly refractive liquid, D_4^{20} 1.6435, n_D^{18} 1.5939, $n_F - n_C$ 0.02333. This yields *lead diethyl dibromide*, glistening prisms, or the dichloride, when treated with the gaseous hydric acids, and these compounds, in turn, give lead dimethyldiethyl when mixed with magnesium methyl iodide solution. J. C. W.

Organo-lead Compounds. P. PFEIFFER, P. TRUSKIER, and P. DISSELKAMP (*Ber.*, 1916, **49**, 2445—2449).—Lead trialkyl haloids can be obtained by the action of the halogen hydrides on lead tetraalkyls (compare lead triethyl chloride, *A.*, 1904, i, 544). In this way, lead tri-*n*-propyl chloride has been prepared independently of Grüttner and Krause (*A.*, 1916, i, 799). When this is shaken with a suspension of silver oxide in water, it gives an alkaline solution of the hydroxide, from which the *bromide*, PbPr_3Br , m. p. 81—82°, the snow-white *sulphate*, and the *acetate*, m. p. 116°, may be obtained. Similarly, *lead tri-n-butyl chloride*, flat needles, m. p. 109—111°, gives an alkaline hydroxide which can be used to prepare the bromide.

Polis's lead diphenyl dichloride, dibromide, and dinitrate (1887) form crystalline *additive compounds* with pyridine in the molecular proportions 1:4, which are similar to the tin compounds, $\text{SnPh}_2\text{X}_2 \cdot 4\text{C}_5\text{H}_5\text{N}$. A compound, $\text{PbPh}_2\text{Br}_2 \cdot 2\text{NH}_3$, also exists.

J. C. W.

New Heterocyclic Systems. III. Organo-lead Compounds. IV. Diethylcyclopentamethyleneplumbine and Products obtained by Rupturing the Ring. GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1916, **49**, 2666—2675).—Through the interaction of lead diethyl dichloride and the magnesium compound of α -dibromo- (or chloro-)pentane, the authors have isolated diethylcyclopentamethyleneplumbine, which thus places lead along with phosphorus, arsenic, antimony, and bismuth among the elements which have been introduced into ring systems during the last two years. When this compound is treated with bromine at -75° , the ring is opened and lead diethyl- ϵ -bromoamyl bromide,



is formed. This reacts with magnesium ethyl bromide to form lead triethyl- ϵ -bromoamyl, which promises to be a very interesting substance, as it contains a reactive group in one of the alkyl radicles, such organo-metallic compounds being hitherto unknown.

The magnesium compound of the α -dihalogenopentane must be free from unchanged magnesium or dihaloid, and the lead diethyl dichloride must be pure (see *A.*, 1916, i, 800). The authors remark that the common prejudice against alkyl chlorides in the Grignard

reaction is really unfounded, for they mostly react quite readily with magnesium that has first been etched.

Diethyleyclopentamethyleneplymbine, $\text{PbEt}_2 \cdot \text{C}_5\text{H}_{10}$, is a colourless, mobile oil, b. p. $111^\circ/13.5$ mm., D_4^{20} 1.6866, n_D^{20} 1.5484, $n_F - n_G$ 0.01770, with an odour reminiscent of cyclohexanone. *Lead diethyl- ϵ -bromoamyl bromide* is a colourless, viscous oil, and *lead triethyl- ϵ -bromoamyl* is a colourless, mobile, stable oil, b. p. $166.8^\circ/13$ mm., D_4^{20} 1.6851, n_D^{20} 1.5374, $n_F - n_G$ 0.01663. This reacts with magnesium, and the magnesium ϵ -triethylplymbylamyl bromide so formed is decomposed by water with the production of *lead triethyl- n -amyl*, an unpleasant smelling, colourless oil, b. p. $121^\circ/15$ mm., D_4^{20} 1.4815, n_D^{20} 1.5095, $n_F - n_G$ 0.01604. The same compound can be synthesised by the action of lead triethyl bromide on magnesium n -amyl bromide.

If the cyclic lead compound is treated with chlorine at -75° , not only is the ring ruptured, but an ethyl radicle is also displaced, and *lead ethyl- ϵ -chloroamyl dichloride* is formed, in doubly-refractive lancets.

Unlike the true lead tetra-alkyls, the cyclic compound is not stable in the air, owing, no doubt, to the considerable tension in the ring.

J. C. W.

The Complexity of some Organic Compounds of Mercury. EINAR BILLMANN and (MLLE.) AGNES HOFF (*Rec. trav. chim.*, 1917, **36**, 289—305).—The authors determine the degree of complexity of the organic mercury compounds by measuring the concentration of the mercury ions in a mixture of a mercury salt and the organic substance giving the organic mercury complex. This has been done in four cases, and from the results the affinities of the reactions have been calculated, using the formula

$$A = R \cdot T \cdot \log K.$$

The comparative results found were:

	<i>c</i> .	<i>K</i> .	<i>A</i> .
Allylacetic acid	$10^{9.29}$	$10^{8.94}$	12493
Allyl alcohol	$10^{8.40}$	$10^{8.10}$	11184
Crotonic acid.....	$10^{5.01}$	$10^{4.71}$	6459
Maleic acid	$10^{3.79}$	$10^{3.47}$	5180

c being the concentration of the mercuric ions, under the uniform conditions, *K* the equilibrium constant, *A* the affinity in gram-calories. Thus the affinity of allylacetic acid and allyl alcohol for the mercury salt is about twice as great as that of crotonic or maleic acid.

W. G.

Some Complex Compounds of Platinum and Mercury. EINAR BILLMANN and (MLLE.) AGNES HOFF (*Rec. trav. chim.*, 1917, **36**, 306—312).—Potassium platinochloride reacts with unsaturated acids, in which the double linking is remote from the carboxyl group, forming complex platinum compounds. When allylacetic acid is added to an aqueous solution of potassium platinochloride a red solution is obtained which, on the addition of ammonium diamminoplatinochloride, gives a yellow, crystalline precipitate of

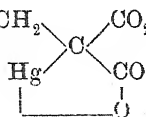
the compound, $(C_3H_5 \cdot CH_2 \cdot CO_2H, PtCl_3)_2Pt(NH_3)_4$. This compound is slowly decomposed on boiling its aqueous solution, and on the addition of potassium platinumchloride gives Magnus's salt.

Allylmalonic acid under similar conditions gives a compound, $[C_3H_5 \cdot CH(CO_2H)_2, PtCl_3]_2Pt(NH_3)_4$,

which is also decomposed on boiling it with water.

Vinylacetic acid under similar conditions gives a yellow, crystalline precipitate, but the constitution of this has not been determined.

When allylmalonic acid (1 mol.) is added to a solution of mercuric acetate (1 mol.) in dilute acetic acid solution a white, crystalline precipitate of *hydroxymercuriallymaleic acid anhydride* (annexed formula) is obtained.



W. G.

Action of Ammonia and Calcium on Benzene. A. V. DUMANSKI and (MLLE.) A. V. ZVEREVA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 994—996).—When dry ammonia is passed through benzene containing shavings of calcium, the following reactions take place: $Ca + 4NH_3 = Ca(NH_3)_4 = Ca(NH_2)_2 + H_2 + 2NH_3$ and $C_6H_6 + H_2 = C_6H_8$.

T. H. P.

The Friedel-Crafts' Reaction. EYVIND BÆDTKER and O. M. HALSE (*Bull. Soc. chim.*, 1916, [iv], **19**, 444—449. Compare Radziewanowski, A., 1895, i, 129, 412).—The inverse of Friedel-Crafts' reaction, $C_6H_5R_2 + 2C_6H_6 \rightleftharpoons 3C_6H_5R$, can be brought about in the case of polyalkylated benzenes by boiling the compound with an excess of benzene and a little aluminium chloride for several hours. The only exceptions found were *m*- and *p*-xylenes, which did not give any toluene. Di- and tri-ethylbenzenes gave ethylbenzene; polyisopropylbenzenes gave isopropylbenzene; *p*-di-*tert*-butylbenzene gave *tert*-butylbenzene; poly-*tert*-amylbenzenes gave *tert*-amylbenzene, and cymene gave excellent yields of toluene and isopropylbenzene.

Attempts to convert dichloro- and dibromo-benzene, under the same conditions, into the monochloro- and monobromo-compounds were entirely unsuccessful, the only products being polyhalogenated benzenes.

W. G.

Electrochemical Chlorination of Benzene and Toluene. FR. FICHTER and LUPU GLANTZSTEIN (*Ber.*, 1916, **49**, 2473—2487).—The chlorination of benzene and toluene at a platinum anode in concentrated hydrochloric acid has received considerable attention, but doubt has been expressed whether the products formed are due to electrochemical action or to the ordinary action of chlorine, particularly as there would seem to be no connexion between the amperage and the yield (see Cohen, Dawson, and Crosland, T., 1905, **87**, 1034; Bruner and co-workers, 1907—1909; van Name and Maryott, A., 1913, ii, 181). It is now suggested that the discordant results

are due to the lack of homogeneity in the electrolyte. Clear solutions can be obtained by adding sufficient glacial acetic acid, and experiments conducted with such electrolytes leave no room for doubt that the chlorination which takes place is really an electrochemical process. Furthermore, under these conditions, it is possible to pursue the chlorination to its utmost limits, but compounds containing oxygen are also produced.

In the case of benzene, the following products have been isolated: chlorobenzene, *p*-dichlorobenzene, *s*-tetrachlorobenzene, hexachlorobenzene, pentachlorophenol, and chloranil. Details are given of experiments on the influence of various factors on the reactions, and the isolation of the products is described. Owing to the complexity of the reactions, there is no connexion between the work done and the quantity of current or the time of the reaction. The best yield of chlorinated products is obtained with a current of 3 faradays, that is, one that provides three gram-atoms of chlorine for every gram-molecule of benzene, and comparative experiments on the influence of other factors were conducted with such a current-quantity. It is found that increasing the concentration of benzene up to the point at which an emulsion is formed (nearly 1 mol. per litre) improves the yield, but the most important factor is the current-density. Raising the amperage up to about 1 amp. per cm.² increases the total yield, and also that of the more chlorinated products, and no hexachlorobenzene is formed at all if the current-density is less than 0.26 amp. per cm.². Higher temperatures are also favourable to the advanced stages of the process. The best conditions for the preparation of hexachlorobenzene are low concentration and higher amperage and temperature, and the solid separates almost completely on cooling in a very pure form. The total yield and yield of hexachlorobenzene are greater at platinum anodes than at those of graphite or magnetic oxide of iron, but at these the oxidation is much more important, about half of the product being soluble in alkali hydroxides.

In the case of toluene, the complexity of the product and the difficulty of isolating the individual compounds are hindrances to a systematic study of the reactions, but the important discovery has been made that, in the dark, at least three chlorine atoms are introduced into the nucleus before the methyl group is attacked. This is taken as very good evidence in support of Bruner's hypothesis that atomic chlorine attacks the ring and molecular chlorine the aliphatic side-chain, and the fact that the electrochemical chlorination is an almost impossible process in the aliphatic series (for example, the acetic acid used in the present mixtures is unaffected) confirms this. The compounds which have been identified, partly by isolation, partly as the products of the action of boiling water on them, are as follows: *o*- and *p*-chlorotoluene, 2:4-dichlorotoluene, 2:4:5-trichlorotoluene; pentachlorotoluene, pentachlorobenzyl chloride, and hexachlorobenzene; 2:4:5-trichlorobenzylidene dichloride (as the corresponding aldehyde) and 2:4:5-trichloro-3:6-dihydroxybenzylidene dichloride, an unstable substance. With a current of 0.005 amp. per cm.², mono- and di-

chlorotoluenes are the sole products; with 0.01 amp. per cm.², trichlorotoluene makes its appearance, but the quinol derivative, which renders the identification of the products so difficult, is not formed until the current density is at least 0.05 amp. per cm.². J. C. W.

Preparation of Nitro-compounds. A. HEINEMANN (Brit. Pat., 102216; from *J. Soc. Chem. Ind.*, 1917, **36**, 78).—Nitrosylsulphonic acid is used in place of concentrated sulphuric acid to absorb the water formed during the nitration of aromatic compounds with nitric acid. Thus *m*-dinitrobenzene (50 grams) is slowly heated with nitrosylsulphonic acid (100 grams) until dissolved; nitric acid (100 grams) is added to the solution, and the mixture is maintained at 110–120° until *s*-trinitrobenzene is formed. H. W.

The Preparation and Ionisation of the Dialkyl Hydrogen Phosphates and Benzenedisulphonic Acids. W. A. DRUSHEL and A. R. FELTY (*Amer. J. Sci.*, 1917, [iv], **43**, 57–66).—Dimethyl, diethyl, and dipropyl hydrogen phosphates were prepared by decomposing the trialkyl phosphates by the action of concentrated aqueous barium hydroxide, purifying the barium tetra-alkyl salts by crystallisation, and treating the anhydrous barium salts with the theoretical quantity of sulphuric acid. From conductivity measurements at 25° it is found that the degree of ionisation of corresponding solutions of the acid esters decreases as the weight of the alkyl group increases.

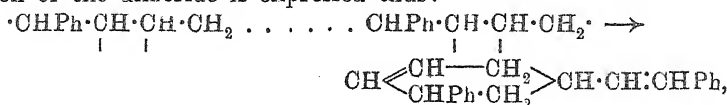
A comparison of the conductivities of the three isomeric benzenedisulphonic acids has shown that in corresponding solutions the para-acid is slightly more ionised than the meta-acid, whilst the ionisation of the ortho-acid is not nearly so great. The rates at which ethyl acetate is hydrolysed by 0.1*N*-solutions of the three acids show differences which correspond with the differences in the degree of ionisation.

The benzene-*o*- and -*p*-disulphonic acids used in these experiments were prepared from the corresponding amino-sulphonic acids by the xanthate method which has been found to give satisfactory results.

H. M. D.

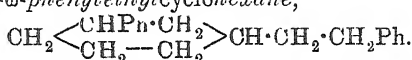
Polymerisation of α -Phenyl- Δ^{γ} -butadiene. S. V. LEBEDEV and A. A. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 997–1008).— α -Phenyl- Δ^{γ} -butadiene polymerises into two products, one soluble, obtained on heating, and the other insoluble, obtained at the ordinary temperature in the light. The results of the author's investigations show that the dimeride of α -phenyl- Δ^{γ} -butadiene is a unicyclic hydrocarbon containing two double linkings; it combines with 2 mols. of hydrogen and with 2 mols. of ozone, and on oxidation with permanganate yields an acid, C₁₃H₁₄O₆, erroneously regarded by Rüber (A., 1904, i, 569) as of the formula C₁₃H₁₂O₆. The character of the polymerisation and the properties of the dimeride and of the polymeride indicate that, in spite of certain individual divergences, the type of the polymerisation is the same as with deriv-

atives of diphenyl with aliphatic substituents. According to the scheme previously given by Lebedev (A., 1913, i, 1285), the formation of the dimeride is expressed thus:



the resulting product being 2-phenyl-4-styrylcyclohexene, and the acid which it gives on oxidation, α -phenylbutane- $\alpha\gamma\delta$ -tricarboxylic acid.

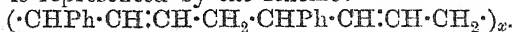
The crude polymeride obtained by heating at 150° is a colourless, viscous liquid, and the dimeride separated by distillation in an atmosphere of hydrogen consists almost entirely of the variety with the higher boiling point. The pure dimeride has b. p. $196.5\text{--}197^\circ/5$ mm., D_4^{20} 1.0332, n_D^{20} 1.59918, n_D^{25} 1.60570, n_F^{20} 1.62346, and when hydrogenated in alcoholic solution in presence of platinum-black yields 1-phenyl-3- ω -phenylethylcyclohexane,



which is a colourless, odourless liquid, b. p. $205\text{--}206^\circ/11$ mm., D_4^{20} 1.0004, n_D^{20} 1.55324, n_D^{25} 1.55787, n_F^{20} 1.56936, n_G^{20} 1.57944. In acetic acid solution complete hydrogenation takes place, the product being the compound, $\text{C}_{20}\text{H}_{36}$, which is a colourless, viscous liquid, b. p. $192^\circ/8.5$ mm., D_4^{20} 0.9257, n_D^{20} 1.49708, n_D^{25} 1.49963, n_F^{20} 1.50573, n_G^{20} 1.46170.

The *diozonide* of the dimeride, $\text{C}_{20}\text{H}_{20}\text{O}_6$, forms a heavy, white powder which flashes when heated. Oxidation of the dimeride with permanganate in acetone solution yields benzoic acid and α -phenylbutane- $\alpha\gamma\delta$ -tricarboxylic acid (compare Thiele and Meisenheimer, A., 1899, i, 603).

The polymeride of α -phenyl- $\Delta^{\alpha\gamma}$ -butadiene, $(\text{C}_{10}\text{H}_{10})_x$, is formed to the extent of 5% at 150° and forms a powdery mass coagulating at about 90° . Its behaviour towards ozone is that of polymerides of divinyl hydrocarbons, the resultant compound, $(\text{C}_{10}\text{H}_{10}\text{O}_4)_x$, being a white solid. The conclusion is drawn that the structure of the polymeride is represented by the scheme:



Experiment shows that compounds containing in the molecule the group $\text{CHPh}\cdot\text{C}\cdot$ are able in the light to form dimerides of the cyclobutane type, and it is highly probable that α -phenyl- $\Delta^{\alpha\gamma}$ -butadiene can yield such a dimeride under suitable conditions, these being a low temperature, diminished velocity of the divinyl type of polymerisation, and action of light.

T. H. P.

Synthetic Investigations in the Indene Series. A. P. ORECHOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 433—449).—This work has been already published in a slightly more condensed form (A., 1914, i, 265).

T. H. P.

Preparation of Aromatic Amines and Catalysts therefor. BADISCHE ANILIN- & SODA-FABRIK (U.S. Pat., 1207802; from *J. Soc. Chem. Ind.*, 1917, 36, 78. Compare A., 1915, i, 796).—The

hydrogen may be mixed with carbon monoxide, and a zinc compound may be used to promote the action of the copper catalyst.

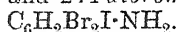
H. W.

The Displacement of Sulphonic Acid Groups in Amino-sulphonic Acids by Halogen Atoms. JOHN JOSEPH SUDBOROUGH and JANIAT VISHINDAS LAKHUMALANI (T., 1917, 111, 41—50).—After summarising the earlier observations of the displacement of such radicles as halogen, carboxyl, acetyl, and sulphonyl by new substituents when in the 2-, 4-, or 6-position with respect to an amino- or hydroxyl group in an aromatic compound, the authors describe the results of an investigation of the action of halogens on various amino-sulphonic and amino-carboxylic acids.

It is found that with 2:6-dibromosulphanilic acid, bromine, applied as bromine water, potassium hypobromite solution, or an acidified solution of potassium bromide or bromate, effects an almost quantitative displacement of the sulphonic acid group with production of *s*-tribromoaniline and sulphuric acid in a yield exceeding 90%; a similar result is obtained with 4:6-dibromoaniline-2-sulphonic acid.

Chlorine reacts with the two isomeric dibromoanilinesulphonic acids, giving mixtures of 4-chloro-2:6-dibromo- and 2-chloro-4:6-dibromo-anilines with tribromoaniline, the formation of the latter probably being due to the displacement of an atom of bromine from one molecule of dibromo-acid and its reaction with a second molecule (compare Wegscheider, A., 1897, i, 557; Chattaway and Orton, T., 1901, 79, 822; Orton and Reed, T., 1907, 91, 1543).

Iodine has no action on the dibromoanilinesulphonic acids even at 100°, but a solution of iodine monochloride in acetic acid effects the displacement of the sulphonic acid group, the products being 2:6-dibromo-4-iodoaniline and 2:4-dibromo-6-iodoaniline,



With the corresponding dibromoaminocarboxylic acids the carbonyl group is more difficult to displace, and whereas bromine gave good yields of *s*-tribromoaniline, chlorine and iodine monochloride effected no displacement in the case of the para- and only a very slight displacement in the case of the ortho-compound.

Comparative experiments showed that a sulphonic acid group in the ortho-position to an amino-group is more reactive than a similar group in the para-position; in the meta-position, a sulphonic acid group is quite inactive towards displacement.

For experimental details see the original paper. D. F. T.

Nitro-derivatives of Alkyltoluidines and the Relation between their Molecular Refractions and those of Similar Compounds. J. D. JANSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, 19, 564—576).—A comparison has been made of the molecular refractivities of a number of nitro-derivatives of aromatic amines, in the course of which some new compounds have been prepared.

2:3-Dinitrodimethyl-*p*-toluidine was obtained by the gradual addi-

tion of 2-nitrodimethyl-*p*-toluidine to excess of nitric acid (D 1·20) in which a little carbamide had been dissolved. After twenty-four hours water was added, and an orange-brown substance separated, which proved to be 2:3-dinitrodimethyl-*p*-toluidine, m. p. 87°. By oxidation with chromic acid it is converted into 2:3-dinitromethyl-*p*-toluidine. By dissolving in nitric acid and adding sodium nitrite it yields 2:3-dinitro-*p*-tolylmethylnitrosoamine, which when boiled with acetic acid gives 2:3-dinitromethyl-*p*-toluidine melting at 159°. Experiments made with ammonia, alkylamines, and aniline show that 2:3-dinitrodimethyl-*p*-toluidine does not react with these substances, and it follows that the nitro-groups are difficult to replace.

2:5-Dinitroethyl-*p*-toluidine is obtained by adding the calculated quantity of nitric acid to diethyl-*p*-toluidine dissolved in concentrated sulphuric acid and pouring into two volumes of water. It has a red colour and melts at 105°. Some 2:5-dinitro-*p*-tolylethyl-nitrosoamine, a light yellow compound melting at 84°, is formed at the same time, the two substances being separated by means of hydrochloric acid.

3:4:5-Trinitro-*o*-tolylethylnitroamine, m. p. 112—113°, is formed when 4-nitroethyl-*o*-toluidine is boiled for some time with nitric acid (D 1·49). It is almost colourless, and forms 3:4:5-trinitroethyl-*o*-toluidine, m. p. 150°, when boiled for some hours with phenol, amyl alcohol, and a little concentrated sulphuric acid.

The refractivity data show that the molecular refraction depends to a considerable extent on the position of the nitro-group with reference to that of the amino-group. If isomerides are arranged in the order of their refractivity, a series is obtained which is identical with the corresponding series for the homologues of these nitro-derivatives except in one case. The exceptional behaviour is shown by the 3:5- and 2:6-dinitro-*p*-toluidines and their dimethyl derivatives. It may be explained by anomalous dispersion, for when the absorption curves for these substances are compared it is found that the curves for the two 2:6-compounds are similar, whilst those for the two 3:5-compounds diverge greatly.

H. M. D.

The Resolution of Asymmetric Quinquevalent Nitrogen Compounds. I. The Salts of *d*- and *l*-Phenylbenzylmethylallylammonium Hydroxide with *d*- and *l*- α -Bromocamphor- π -sulphonic Acid. JOSEPH REILLY (T., 1917, 111, 20—28).—The optically active acids show greater variation with regard to the facility with which they can be employed as agents for the resolution of compounds containing asymmetric nitrogen atoms than for the resolution of similar carbon compounds. After briefly reviewing the different behaviour of the optically active acids in this respect and indicating the possible reasons why in the case of some racemic bases salt formation with certain optically active acids does not give a product capable of resolution by recrystallisation, the author describes experiments made with the phenylbenzylmethylallylammonium bromocamphorsulphonates.

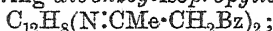
Whereas *dl*-phenylbenzylmethylallylammonium iodide (Pope and

Peachey, T., 1899, 75, 1127) is easily resolvable by conversion into the *d*- or *l*-camphorsulphonate, the substitution of α -bromocamphor- π -sulphonic for camphorsulphonic acid gives a much less satisfactory result. In order to ascertain whether racemisation sufficiently accounts for this difference, the author has obtained pure *d*-phenylbenzylmethylallylammonium *d*- α -bromocamphor- π -sulphonate and *l*-phenylbenzylmethylallylammonium *l*- α -bromocamphor- π -sulphonate, $[\alpha]_D + 81.5^\circ$ and -81.2° respectively, by the interaction of the iodide of the necessary base with the silver salt of the correct acid. In a similar manner, *d*-phenylbenzylmethylallylammonium *l*- α -bromocamphor- π -sulphonate and *l*-phenylbenzylmethylallylammonium *d*- α -bromocamphor- π -sulphonate, $[\alpha]_D - 20.5^\circ$ and $+ 20.3^\circ$ respectively, were prepared from the corresponding iodides and silver salts. These four salts are of the same order of stability as the corresponding β -camphorsulphonates and show very little tendency to racemise; it is therefore unlikely that racemisation is the cause of the relative difficulty of resolving *dl*-phenylbenzylmethylallylammonium iodide by means of the active α -bromocamphor- π -sulphonic acids.

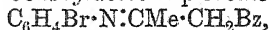
For experimental details see the original paper.

D. F. T.

Studies in Ring Formation. II. The Action of Aromatic Amines on Acetylacetone and Benzoylacetone. EUSTACE EBENEZER TURNER (T., 1917, 111, 1—4. Compare A., 1915, i, 1052).—Benzoylacetone behaves similarly to acetylacetone (*loc. cit.*) towards benzidine, giving *dibenzoylisopropylidenebenzidine*,



it also reacts with α - and β -naphthylamines, *p*-bromoaniline, and 2:6-dimethoxyaniline, forming the corresponding mono-anils, namely, *benzoylacetone- α -naphthalide*, *benzoylacetone- β -naphthalide*, $C_{10}H_7\cdot N:CMc\cdot CH_2Bz$, *benzoylacetone-*p*-bromoanil*,



and benzoylacetone-2:6-dimethoxyanil respectively; diphenylamine is without action on benzoylacetone. The mono-anil of benzoylacetone (Beyer, A., 1887, 849) refuses to condense further with aniline, whilst the mono-anil derived from acetylacetone when heated with aniline yields no dianil, but undergoes disruption with formation of acetanilide; diacetylisopropylidenebenzidine, the condensation product of acetylacetone and benzidine, also appears to be unaffected by boiling aniline.

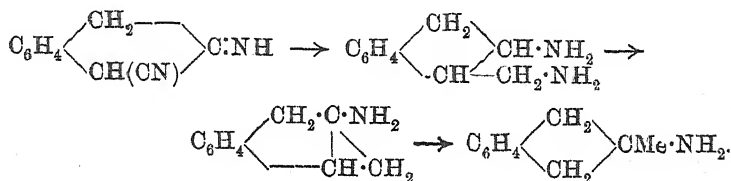
The behaviour of β -diketones is thus seen to be very different from that of α -diketones which fairly readily yield dianils, and it also appears that the mechanism of the interaction of a β -diketone, such as benzoylacetone with the reagents mercaptan, aniline, and semicarbazide, is different in each case (see Posner, A., 1901, i, 14).

For experimental details see the original.

D. F. T.

The Indene Series. III. 2-Amino-2-methylhydrindene from *o*-Xylylene Dicyanide. J. VON BRAUN, O. KRUBER, and E. DANZIGER (*Ber.*, 1916, 49, 2642—2654).—In 1892, Zanetti obtained the expected diamine, $C_6H_4(CH_2\cdot CH_2\cdot NH_2)_2$, and another

base, $C_{10}H_{13}N$, by the reduction of *o*-xylylene dicyanide by means of sodium and alcohol. The authors anticipated that this base would contain a seven-membered ring, and be formed, therefore, by the elimination of ammonia from the diamine, as piperidine is formed from pentamethylenediamine. On investigation, however, they find that it is a primary amine, contains no ethylene linking, yields phthalic acid on oxidation, is not a tetrahydronaphthylamine, and consequently, neither of the more obvious compounds, but rather 2-amino-2-methylhydrindene. Moore and Thorpe have shown that *o*-xylylene dicyanide is readily transformed by alkalis into a cyclic iminonitrile (T., 1908, 93, 165), and it is now found that this compound also yields the above base on reduction. It appears, therefore, that the dicyanide is either reduced directly to the diamine or first rearranged and then reduced when boiled with sodium and alcohol. Even so, the whole reduction is remarkable, and it seems to be without a parallel. The reduction of the iminonitrile is explained by the scheme:



The two bases obtained by boiling *o*-xylylene dicyanide, in quantities as large as 100 grams at a time, with sodium and alcohol, are easily separated by distillation. *o*-Di- β -aminoethylbenzene is a colourless, almost odourless liquid, b. p. 165–170°/18 mm., which forms a *platinichloride*, a *picrate*, m. p. 219–220°, an *acetyl* compound, m. p. 190°, and a *benzoyl* derivative, m. p. 201°. It behaves in many respects more like ethylenediamine than a polymethylenediamine, giving, for example, with methyl iodide, only the *compound*, $\text{NMe}_3 \cdot \text{C}_2\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_2\text{H}_4 \cdot \text{NMe}_3\text{I}$, m. p. 175–185°, and not yielding a glycol on treatment with nitrous acid. It is furthermore remarkable that this glycol cannot be obtained by the other method, namely, by the reduction of the ester of the corresponding acid. *o*-Phenylenediacetic acid can be prepared readily by heating *o*-xylene dicyanide with concentrated hydrochloric acid at 110° in a sealed tube, and the *ethyl* ester, $\text{C}_6\text{H}_4(\text{CH}_2\text{CO}_2\text{Et})_2$, has b. p. 188°/15 mm. The base is also physiologically inert, which would not be expected from its relationship to β -phenylethylamine.

2-Amino-2-methylhydrindene is an oil with a mild basic odour, has b. p. 118–119°/18 mm., and yields the following derivatives: *hydrochloride*, m. p. 241°, *hydrobromide*, m. p. 290–293°, *platinichloride*, decomp. 220°, *picrate*, m. p. 244°, *benzoyl* derivative, m. p. 160°, and *acetyl* compound, m. p. 127°. The *benzenesulphonyl* compound, m. p. 104°, reacts with methyl iodide in the presence of sodium ethoxide to form 2-benzenesulphonylmethylamino-2-methylhydrindene, m. p. 93–95°, which may be hydrolysed to 2-methylamino-2-methylhydrindene, b. p. 113–118°/15 mm. (*hydrochloride*,

m. p. 212°, *platinichloride*, m. p. 197°, dark yellow *picrate*, m. p. 196—198°, *benzoyl* derivative, m. p. 95—97°. This secondary base yields the *quaternary ammonium iodide*, $C_6H_4 \begin{smallmatrix} <CH_2> \\ <CH_2> \end{smallmatrix} CMe \cdot NMe_3I$, m. p. 227°, more readily than the primary amine. 2-Methyl-2-hydrindylphenylthiocarbamide, m. p. 180°, and di-2-methyl-2-hydrindylthiocarbamide are readily obtained, and the base also condenses easily with aldehydes, the *salicylidene* compound having m. p. 92°.

The base is smoothly transformed into 2-chloro-2-methylhydrindene, a faintly, pleasant smelling oil, b. p. 112—114°/15 mm., by distilling its benzoyl derivative with phosphorus pentachloride. This, or, better, the above quaternary ammonium iodide, can then be converted into 2-methylindene, $C_6H_4 \begin{smallmatrix} <CH_2> \\ <CH> \end{smallmatrix} CMe$, which has b. p. 184—185°/741 mm., D_4^{20} 0.9897, n_D^{20} 1.57574, and forms a well-crystallised *anisylidene* compound, m. p. 120°. The production of 2-hydroxy-2-methylhydrindene from the amine or chloro-compound is attended by difficulties which have not been overcome, but the compound can be synthesised by the action of magnesium methyl iodide on β -hydrindone. It has m. p. 52°, b. p. 132—135°/11 mm., and forms a *benzoate*, m. p. 145°.

2-Amino-2-methylhydrindene has remarkable physiological properties. It increases the blood pressure more than β -phenylethylamine, and, when injected subcutaneously, causes excitation of the motory nerve and respiratory centres in a very high degree.

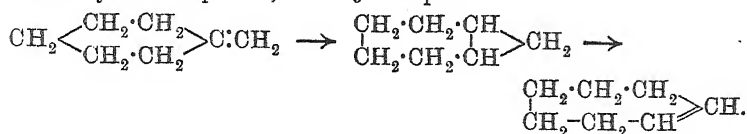
J. C. W.

Isomeric Transformations in the Series of cycloHexanol and its Homologues and of cycloHexylcarbinol. N. A. ROZANOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 309—321. Compare A., 1915, i, 657).—The author has investigated the action of hydriodic acid at a low temperature on cyclohexanol, cyclohexylcarbinol, 1-methyl-4-cyclohexanol, and 1-methyl-3-cyclohexanol, the action of silver nitrite on the iodides obtained, and the action of oxalic acid or acetic anhydride on the alcohols, with the object of ascertaining in which stage and under what conditions phenomena of isomerisation occur.

The action of hydriodic acid on cyclohexanol yields solely cyclohexyl iodide, which is converted by silver nitrite into a mixture of nitrocyclohexane and 1-nitro-1-methylcyclopentane. In the action of either aqueous or anhydrous oxalic acid on cyclohexanol, no isomerisation takes place, almost quantitative yields of cyclohexene being obtained. cycloHexylcarbinol is convertible into the corresponding iodo-derivative, and the latter, by the action of oxygen on the magnesium compound, back again into the alcohol without isomerisation. The action of silver nitrite on this iodide, namely, ω -iodomethylcyclohexane, yields ω -nitromethylcyclohexane and 1-nitro-1-methylcyclohexane (compare Zelinski, A., 1908, i, 864).

The action of oxalic acid on cyclohexylcarbinol yields methylene-

cyclohexane, which undergoes further change, presumably by way of a bicyclic compound, into *cycloheptene*:



The conclusion is drawn that six-membered rings are little, if at all, more stable than those with five carbon atoms. The isomerising factors are here, also, (1) the action of halogen hydracid, but only at a high temperature, (2) nitration by means of silver nitrite, and (3) the action of oxalic acid. In the last case, this effect is exerted only at the moment of the reaction and only with primary alcohols, that is, with derivatives of carbinol. As with other rings, isomerisation of compounds with a side-chain is accompanied by enlarging of the ring, whilst that of compounds without a side-chain produces diminution of the ring.

The action of silver nitrite on 2-iodo-1-methyl*cyclohexane* yields 1-nitro-1 : 2-dimethylcyclopentane, $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CMe} \cdot \text{NO}_2 \\ \text{CH}_2 \cdot \text{CHMe} \end{array}$, b. p. 72—75°/45—46 mm., D_4^{20} 1.0310, n_D^{20} 1.4538; the normal product of the reaction was not obtained pure, owing to insufficiency of material. This action and that of silver nitrite on 3-iodo-1-methyl*cyclohexane* are under investigation. T. H. P.

Nitration of *p*-Tolyl Carbonate. A. F. HOLLEMAN and (MLLE.) J. M. A. HOEFLAKE (*Rec. trav. chim.*, 1917, **36**, 271—280).—A quantitative study of the nitration of *p*-tolyl carbonate in sulphuric acid at 4—9°. The results show that the nitro-group enters as 96.3% in the ortho-position to the methyl group and 3.7% into the meta-position, thus indicating that the influence of the carbonate group is infinitely small in comparison with that of the methyl group. W. G.

Tetra- and Penta-methylorcinol. II. J. HERZIG and F. WENZEL (*Monatsh.*, 1916, **37**, 549—565. Compare A., 1911, i, 776).—The earlier portion of the paper is devoted to a discussion of the probable structure of the bromo-derivatives $\text{C}_{11}\text{H}_{14}\text{O}_2\text{Br}_2$ and $\text{C}_{12}\text{H}_{17}\text{O}_2\text{Br}$ obtained, respectively, from tetramethyl- and pentamethyl-orcinol; the former derivative, on treatment with potassium hydroxide, yields a mixture of fumaric acid and diisopropyl ketone, whilst the latter gives a substance of the composition $\text{C}_{13}\text{H}_{18}\text{O}_3$ (*loc. cit.*). The chemical behaviour of this substance (see below) does not supply sufficient evidence to enable a final choice of structure, and two alternative schemes of formulation are suggested to represent the relationship with pentamethyl-orcinol.

[With ST. EBERWEIN.]—Although the substance $\text{C}_{12}\text{H}_{18}\text{O}_3$ is soluble in potassium hydroxide solution without decomposition and can be recovered unchanged, prolonged treatment with boiling

potassium hydroxide solution causes the formation of two substances, one a neutral oil, $C_{11}H_{18}O$, b. p. 102—103°/15 mm., and the other a crystalline acid, $C_{11}H_{20}O_4$, m. p. 133—135° (the *methyl ester*, m. p. 38—40°, forms an *acetyl derivative*). D. F. T.

***o*- and *p*-Triphenetyltelluronium Salts.** KARL LEDERER (*Ber.*, 1916, 49, 2529—2531).—Compare other triaryltelluronium salts (*A.*, 1916, i, 810). The new *p*- and *o*-triphenetyltelluronium salts are, respectively, as follows: *iodides*, rhombic needles, m. p. 208—209°, and white needles, m. p. 226—227°; *bromides*, m. p. 218° and m. p. 202—203°; *picrates*, elongated, rhombic plates, m. p. 178—179°, and cubes, m. p. 164—165°. J. C. W.

***o*-Phenetyltellurium Compounds.** KARL LEDERER (*Ber.*, 1916, 49, 2532—2538).—Di-*o*-phenetyl telluride has been obtained by the action of magnesium *o*-phenetyl bromide on tellurium dibromide (compare *A.*, 1916, i, 208). It is not identical with the Rust-Rohrbaech product of the action of tellurium tetrachloride on phenetole (*ibid.*).

Di-*o*-phenetyl telluride, $Te(C_6H_4 \cdot OEt)_2$, is a viscous oil, b. p. 244—244.5°/18 mm., which gives rise to the following di-*o*-phenetyltelluronium compounds in the usual way; *dichloride*, columns, m. p. 163—164°; *dibromide*, four-sided columns, m. p. 183—184°; *diiodide*, deep reddish-brown needles or rhombic tablets, m. p. 214—215°; *oxide*, $TeO(C_6H_4 \cdot OEt)_2$, short needles, m. p. 205—206°, easily oxidised by the air during its crystallisation; *methiodide*, columns, m. p. 138—140°. It also forms *additive compounds* with the mercuric haloids, as follows: *chloride*, $Te(C_6H_4 \cdot OEt)_2 \cdot HgCl_2$, m. p. 174—175°; *bromide*, m. p. 160—161°; *iodide*, m. p. 90°. J. C. W.

***a*-Naphthyltellurium Compounds.** KARL LEDERER (*Ber.*, 1916, 49, 2663—2666).—Di-*a*-naphthyl telluride was obtained by Lyons and Bush by heating tellurium with mercury di-*a*-naphthyl (*A.*, 1908, i, 417), but it may also be obtained by the author's general method, namely, by the action of magnesium *a*-naphthyl bromide on tellurium dibromide. It forms *additive compounds* with the mercuric haloids: *chloride*, m. p. 187—188° (decomp.); *bromide*, m. p. 178—179°; *iodide*, yellow granules, m. p. 152—153° (decomp.). Di-*a*-naphthyltelluronium di-*iodide* crystallises in deep red needles, m. p. 184—186°; the *oxide*, R_2TeO , is a microcrystalline powder, m. p. 224—225° (decomp.), and di-*a*-naphthylmethyltelluronium iodide has m. p. 146° (decomp.). J. C. W.

***p*-Hydroxytolylsulphone.** JOSEF ZEHENTER (*Monatsh.*, 1916, 37, 587—607. Compare *A.*, 1912, i, 444).—When *p*-cresol is heated with fuming sulphuric acid at 170—180° for four to six hours, *p*-hydroxytolylsulphone (compare Tassinari, *A.*, 1889, 245) is formed, together with a small quantity of di-*p*-tolyl oxide and a larger quantity of 4-cresol-2-sulphonic acid. The following derivatives of the sulphone were prepared: *sodium derivative*,

$C_{14}H_{13}O_4SNa \cdot 3\frac{1}{2}H_2O$, microscopic prisms; *potassium* derivative, not obtained crystalline; *dibenzoyl* derivative, $C_{14}H_{12}O_4SBz_2$, needles, m. p. 231—232°; *dibromo*-derivative, $C_{14}H_{12}O_4Br_2S$, colourless prisms, m. p. 185—188°; *dinitro*-derivative, $C_{14}H_{13}O_4S(NO_2)_2$, obtained by the action of diluted nitric acid (1:1), m. p. 222—224°; *disulphonic* acid with $6H_2O$, which could not be dehydrated further than $C_{14}H_{12}O_4S(SO_3H)_2 \cdot H_2O$, m. p. 156—158° (*potassium* salt with $4H_2O$, colourless leaflets; *sodium* salt with $5H_2O$, colourless, microscopic prisms; *barium* salt with $6H_2O$, of which only five were removable without decomposition of the salt; *lead* salt with $5H_2O$), obtained from the sulphone by the action of sulphuric acid at 100°.

When heated with sulphuric acid at 180°, the sulphone was converted into 4-cresol-2(or 6):3-disulphonic acid (Richter, A., 1886, 151).
D. F. T.

Diaryldisulphones. O. HINSBERG (*Ber.*, 1916, 49, 2593—2594).—Kohler and MacDonald (A., 1899, i, 904) found that the same product is obtained by treating sodium benzenesulphinate with *p*-toluenesulphonyl chloride as by the action of benzenesulphonyl chloride on sodium *p*-toluenesulphinate, and regarded this fact as evidence of the formula $R \cdot SO_2 \cdot SO_2 \cdot R$ for diaryldisulphones. This is supported by the preparation, in either direction, of *phenyl-β-naphthyl*disulphone, $C_{10}H_7 \cdot SO_2 \cdot SO_2 \cdot Ph$, which crystallises in clusters of colourless needles, m. p. 166°. J. C. W.

Reaction of Ethereal Complexes of Metal Haloids with Aromatic Hydrocarbons. I. N. S. COŇEV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 550—580).—The aim of the author's investigations is to procure new experimental data capable of elucidating the structure of the etherates, and the present paper contains the result of work on the etherates of stannic chloride. Emphasis is laid on the necessity of investigating the etherates in conditions which exclude the possibility of any decomposing action of atmospheric moisture. With this end in view, a special apparatus, to be described later, has been devised.

With ethyl ether, stannic chloride always forms the dietherate, $SnCl_4 \cdot 2Et_2O$, m. p. 87°, no matter what the experimental conditions employed. When heated on a water-bath, the etherate decomposes into ether and stannic chloride, but at 113° its decomposition yields, in addition, ethyl chloride. Ethyl propyl ether forms only the dietherate, and the same is the case with propyl ether; the compound obtained with the latter does not give the expected results on dry distillation, and this reaction is being further investigated. *iso*Amyl ether also gives a dietherate, $SnCl_4 \cdot 2(C_5H_{11})_2O$, which decomposes into its components on distillation.

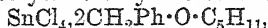
Benzyl ethyl ether always yields the unstable, hygroscopic dietherate, $SnCl_4 \cdot 2CH_2Ph \cdot OEt$, which can only be kept undecomposed in excess of benzyl ethyl ether. Spontaneous decomposition of this dietherate gives alcohol and a hydrocarbon, $(C_7H_8)_n$, m. p.

72—75° (decomp.), which has the molecular formula $(C_7H_6)_{31}$, in freezing benzene. That this hydrocarbon is a product of the condensation of the benzyl radicle alone is shown by its formation by the action of stannic chloride on benzyl chloride (compare Zincke, A., 1871, 508, 688). It is therefore probable that benzyl chloride is an intermediate product of the decomposition of the benzyl ethyl etherate, but this could not be confirmed by direct experiment. In similar experiments with titanium chloride in place of stannic chloride, benzyl chloride was, however, isolated, and that this decomposition actually follows the above course is shown by the products it yields in presence of benzene and toluene; with the latter, the benzyl chloride formed gives the corresponding hydrocarbons. The compounds obtained in presence of benzene are: diphenylmethane, *p*- and *m*-dibenzylbenzenes, alcohol, and the compound $SnCl_4 \cdot C_6H_5Et$; that these hydrocarbons owe their formation to the intermediate formation of benzyl chloride is shown by the fact that they are obtained by the interaction of stannic chloride and benzyl chloride in benzene.

Decomposition of the benzyl ethyl etherate in toluene solution gives *p*-benzyltoluene, one or more of the isomeric dibenzyltoluenes in small proportion, and alcohol.

Benzyl methyl ether always yields the unstable dietherate, $SnCl_4 \cdot 2CH_3Ph \cdot OMe$, which yields the hydrocarbon, $(C_7H_6)_n$, m. p. 73—76° (decomp.), on decomposition. When heated in benzene solution, this dietherate decomposes, giving diphenylmethane, *p*-dibenzylbenzene, and a viscous oil and an amorphous solid, which were not further investigated.

Benzyl *iso*amyl ether yields only the dietherate,



which is stable at the ordinary temperature, but when heated undergoes decomposition in the same way as the corresponding compounds of benzyl ethyl and benzyl methyl ethers, yielding the hydrocarbon, $(C_7H_6)_n$, m. p. 72—75° (decomp.). When heated in benzene solution, this etherate decomposes, yielding *iso*amyl alcohol, diphenylmethane, *p*-dibenzylbenzene, and a hydrocarbon which has a high boiling point and is similar to those obtained in other cases.

When heated in benzene solution, the etherate formed from stannic chloride and benzyl benzoate decomposes, giving diphenylmethane, *p*-dibenzylbenzene, benzoic acid, and hydrocarbons of high molecular weight.

T. H. P.

Reaction of Esters with Organo-magnesium Compounds.

IV. G. L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 297—300).—The interaction of ethyl benzoate and magnesium phenyl bromide is analogous to that of methyl or benzyl benzoate (A., 1916, i, 259); if the cooling is insufficient and the whole of the ester is added at once to the organomagnesium compound, the reaction does not cease at the formation of the iodomagnesium triphenylmethoxide, but proceeds further in the direction of the formation of triphenylmethyl ethyl ether.

As would be expected from the course followed by the action of

ethyl acetate on the iodomagnesium alcoholate of benzhydrol (compare A., 1915, i, 957), the action of ethyl acetate on iodomagnesium triphenylmethoxide yields triphenylmethyl ethyl ether, but in very small yield, most of the triphenylcarbinol used being recovered unchanged; in the former reaction, both dibenzhydrol ether and benzhydrol ethyl ether are obtained, the whole of the benzhydrol reacting in these directions. This difference in behaviour in the two cases is due to the fact that the iodomagnesium alcoholate of benzhydrol is deposited as a microcrystalline powder when magnesium ethyl iodide acts on benzhydrol, and redissolves on addition of ethyl acetate (2 mols.), whereas the iodomagnesium triphenylmethoxide does not pass into solution again even when treated with a large proportion of ethyl acetate. A still lower yield of triphenylmethyl ether is obtained if the reaction is carried out in a mixture of absolute ether and benzene. T. H. P.

The Catalytic Decomposition of Benzoyl Chloride. ALPH. MAILHE and F. DE GODON (*Bull. Soc. chim.*, 1916, [iv], 19, 449—452).—When benzoyl chloride in a current of hydrogen is passed over finely divided nickel at 270—280°, there is an abundant liberation of hydrogen chloride, and the products are benzene, toluene, and diphenyl, the formation of the latter being due to the catalytic action of the nickel chloride produced. Finely divided copper under similar conditions gives benzoic anhydride, 40%, and unchanged benzoyl chloride, 60%. Barium chloride or thorium oxychloride at 420—450° give 25% of benzoic anhydride and 70% of unchanged benzoyl chloride. These two catalysts blacken, but can be regenerated by calcination. W. G.

Some Derivatives of Amino-acids. J. TH. BORNWATER (*Rec. trav. chim.*, 1917, 36, 281—284).—*Ethyl benzoyl-d-aminovalerate*, $\text{NHBz} \cdot [\text{CH}_2]_4 \cdot \text{CO}_2\text{Et}$, m. p. 26°, is readily obtained by passing dry hydrogen chloride into a solution of the free acid in absolute alcohol. When shaken with a 25% solution of ammonium hydroxide, it gives the corresponding *amide*, m. p. 181·5°.

Benzoyl-*d*-diaminovaleric acid gives in alcoholic solution with dry hydrogen chloride its *ethyl ester hydrochloride*.

Ethyl chloroacetylaspartate (compare Fischer and Suzuki, A., 1905, i, 121) is readily obtained by boiling chloroacetyl chloride and ethyl aspartate hydrochloride together in dry benzene solution. W. G.

Menthanecarboxylic Acids. N. I. KURSANOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 862—867. Compare A., 1915, i, 420).—With the object of determining the composition of crude menthyl chloride, the author has made a preliminary examination of the menthanecarboxylic acids.

The constant menthyl chloride yields only one menthanecarboxylic acid, m. p. 65—66°, whilst crude menthyl chloride gives also a liquid acid. The action of phosphorus trichloride on the crystalline acid causes no stereoisomeric transformation, since the chloroanhydride formed may be converted again into the original acid.

Menthanecarboxylic acid, m. p. 65—66°, $[\alpha]_D -54\cdot23^\circ$ (in benzene), yields the crystalline amide, $\text{C}_{10}\text{H}_{19}\cdot\text{CO}\cdot\text{NH}_2$, m. p. 151°,

$[\alpha]_D -56.47^\circ$ (in methyl alcohol), which forms stout, prismatic crystals of the composition $(C_{11}H_{21}ON)_2 \cdot C_6H_6$; this is the only amide formed by the crystalline acid, which also gives only one anilide, $C_{11}H_{25}ON$, m. p. 152° , $[\alpha]_D -70.46^\circ$.

The liquid menthanecarboxylic acid obtained, together with the crystalline acid from crude menthyl chloride, has also been examined, but the results as yet available are insufficient to decide if the liquid acid is an individual compound or a mixture of isomerides.

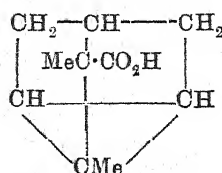
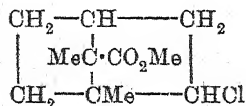
T. H. P.

An Isomeric Teresantalic Acid. H. RUPE and W. TOMI (*Ber.*, 1916, **49**, 2563—2579).—Teresantalic acid, which has been fairly completely studied by von Soden and Müller (A., 1900, i, 678), Guerbet (A., 1900, i, 242), and later by Semmler (A., 1907, i, 703, 1062; 1910, i, 573; 1911, i, 314), is of interest to the authors in connexion with work on the dependence of rotatory power on constitution. They hope to study the changes in rotation which take place as the tricyclic acid is transformed into simpler ring systems. As a preliminary, they have attempted to obtain an unsaturated acid by removing the elements of hydrogen chloride from the product of the addition of this acid to methyl teresantalate, but they have only succeeded thereby in preparing a saturated isomeride of teresantalic acid, which they designate *isoteresantalic acid*. Based on the "camphor-type" formula for teresantalic acid, the explanation offered is that the carboxyl group and the methyl group attached to the same carbon atom merely exchange positions, the former being in one case within the space bounded by the rings and outside it in the other.

Methyl teresantalate was originally obtained by the action of methyl iodide on the silver salt. Other esterification methods have now been tried in order to prepare larger quantities. For example, the *acid chloride*, b. p. $100-104^\circ/14$ mm., has been isolated by the action of thionyl chloride, but the tendency for the acid to combine with hydrogen chloride is so great that this does not give a satisfactory ester. The application of methyl

sulphate, however, is quite successful. Methyl teresantalate combines with hydrogen chloride in cold alcoholic solution to form *methyl hydrochloroteresantalate* (annexed formula), which exists in two forms, α -, white leaflets, m. p. 68° , b. p. $125-127^\circ/10$ mm., and β -, which is liquid. The corresponding *methyl hydrobromoteresantalate* is a pale yellow syrup. When these esters (better, the bromo-

ester) are heated with aniline at $200-210^\circ$ they yield *methyl isoteresantalate*, b. p. $93.5-94.5^\circ/10$ mm., from which *isoteresantalic acid* (annexed formula) is obtained by hydrolysis with alcoholic potassium hydroxide, in white crystals, m. p. 141.5° , b. p. $145-155^\circ/12$ mm. The same acid is obtained when the hydrochloroteresantalates are boiled with alco-



holic potassium hydroxide, or when the hydrobromoteresantalate is treated with zinc dust and acetic acid. The ordinary teresantallic acid, m. p. 155°, is not changed by boiling with quinoline or aniline, but the *iso*-acid loses carbon dioxide and is also partly converted into the ordinary acid. The *iso*-acid is also more soluble in water than the older acid. *Calcium, strontium, and barium* salts of each acid have been prepared.

Other experiments of a less conclusive nature are recorded. Methyl teresantalate yields a *dibromide*, without the formation of hydrogen bromide. *Teresantanilide*, b. p. 204—205°/11 mm., is formed as a by-product in the action of aniline on methyl hydrobromoteresantalate; it changes into an *isomeride*, large, white spears, m. p. 84—86°, when boiled with alcoholic hydrochloric acid.

The chief optical constants quoted are tabulated below, choice being made of those which the authors regard as most trustworthy:

	$[\alpha]_D^{20}$	$\lambda\alpha$
Teresantalic acid (benzene solution)...	-76.60°	684.7 $\mu\mu$
Teresantalic acid methyl ester	-60.78	679.6
<i>iso</i> -Teresantalic acid (benzene)	-127.58	640.0
<i>iso</i> -Teresantalic acid methyl ester.....	-108.75	641.0
Methyl hydrochloroteressantilate (α - form. in benzene)	-9.22	655.0

J. C. W.

The Stereochemistry of Quinquevalent Nitrogen. V. The Betaines and the Formation of Unsaturated Acids in Plants. I. SHIGERU KOMATSU (*Mem. Coll. Sci. Kyoto*, 1916, 1, 369—390).—The unsaturated acids in plants, with the exception of certain fatty acids, are α -unsaturated compounds, and are associated with alkaloids or tertiary amines. This accords with their formation by the decomposition of betaines.

Ethyl phenyldimethylammonium acetate iodide, prepared from dimethylaniline and ethyl iodoacetate, decomposes at 103–105° and then solidifies to a mass of phenyltrimethylammonium iodide.

Benzylmethylaniline and ethyl iodoacetate yield ethyl phenylbenzylmethylanmoniumacetate iodide, m. p. 115–116°. When dissolved in acetone and ethyl acetate and heated with silver *d*-camphorsulphonate on the water-bath for two hours, the *d*-camphorsulphonate of the base is obtained in white crystals of m. p. 178–179°, giving in aqueous solution $[\alpha]_D^{25} + 13.68^\circ$. The corresponding *d*-bromide has m. p. 139–140°.

Pyridine and *l*-menthyl iodoacetate yield the *l*-iodide,
 $\text{C}_{10}\text{H}_{19}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{NC}_5\text{H}_5\text{I}$,
 m. p. 178—179°, $[\alpha]_D^{25} - 62.17^\circ$.

Benzylmethylaniline and *l*-menthyl iodoacetate yield phenyldibenzylmethylanmonium iodide, m. p. 108.5–109°. The corresponding platinichloride has m. p. 137–138°.

The betaine, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \underset{\text{NMe}_3 \cdot \text{O}}{\text{CH}} \cdot \text{CO}$ obtained by the methylation of tyrosine, forms a *picrate* melting at 171—172°. The betaine

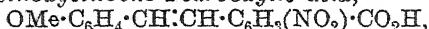
decomposes on heating into *p*-methoxycinnamic acid and trimethylamine. The betaine, $\text{CH}_2\text{Ph}\cdot\text{CH}-\overset{\text{O}}{\overset{\text{NMe}_3}{\text{C}}}-\text{CO}$, prepared by methylating phenylalanine, forms a *picrate* of m. p. 162—163° and decomposes into cinnamic acid and trimethylamine on heating.

The methylation of α -aminobutyric acid yields the betaine, $\text{CH}_2\text{Me}\cdot\text{CH}-\overset{\text{O}}{\overset{\text{NMe}_3}{\text{C}}}-\text{CO}$, the *picrate* of which melts at 155—156°, whilst the betaine decomposes into α -crotonic acid and trimethylamine on heating.

Methyl iodide and potassium hydroxide convert aspartic acid into fumaric acid, trimethylamine being also formed. C. H. D.

The Border-line between Isomerism and Polymorphism. II. PAUL PFEIFFER [with J. KLINKERT and A. VON POLLITZER] (*Ber.*, 1916, 49, 2426—2441. Compare A., 1916, i, 24).—In the earlier paper a number of nitromethoxystilbenes were described which exist in the solid state in yellow and orange forms. It now appears that two forms are only given, apparently, when the methoxyl (or a hydroxyl) group is in the para-position. As the two solids have the same melting point and give the same colour in solution, they would be regarded as dimorphic forms were it not that in many cases different additive compounds are produced by the two modifications. The most striking example of this is 2-nitro-4'-methoxystilbene-4-carboxylic acid. The yellow acid gives an orange-coloured pyridine salt, and the orange acid gives a yellow pyridine salt, the acids being recoverable by means of hydrochloric acid. In fact, it is possible to pass through a cycle of changes, thus: the yellow acid forms an orange salt which changes into the yellow salt on treatment with an excess of pyridine (owing to partial solution taking place), and this yellow salt yields the orange acid, which changes into the yellow acid on heating. The kind of isomerism here exhibited cannot be explained by the prevailing theories, and is termed "cryptoisomerism."

2-Nitro-2'-methoxystilbene-4-carboxylic acid,



from the corresponding nitrile (*ibid.*, p. 26) is a greenish-yellow powder, m. p. 230°, which forms a pale yellow potassium salt, $1\text{H}_2\text{O}$, a pyridine salt, flat, transparent, yellow needles, and additive compounds with acetic acid, golden-yellow needles, and dichloroacetic acid, golden-yellow leaflets. 4-Nitro-2-cyano-2'-methoxystilbene, from *p*-nitro-*o*-toluonitrile and *o*-methoxybenzaldehyde, crystallises in golden needles, m. p. 146—148°. 2-Nitro-4-cyano-3'-methoxystilbene, from *o*-nitro-*p*-toluonitrile and *m*-methoxybenzaldehyde, forms greenish-yellow, glistening needles, m. p. 163—164°, and may be hydrolysed to 2-nitro-3'-methoxystilbene-4-carboxylic acid, yellow needles, m. p. 240°, which gives an orange-yellow potassium salt, $0.5\text{H}_2\text{O}$, and a golden-yellow sodium salt, $2\text{H}_2\text{O}$.

The yellow and red pyridine salts of 2-nitro-4'-methoxystilbene-4-carboxylic acid (*ibid.*) are described above. The acid also forms yellow aniline, quinoline, and diethylamine salts, which give the

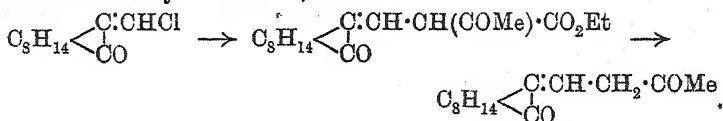
orange-coloured forms of the acid on treatment with hydrochloric acid.

4-Nitro-4'-methoxystilbene-2-carboxylic acid, from the nitrile (*ibid.*), crystallises in golden-yellow, glistening needles, m. p. 215°, combines with H_2O , forms a barium salt, golden needles, a potassium salt, yellow leaflets, and gives two pyridine salts, a yellow variety (acid to base=1:1) crystallising from cold solutions in the base, and an orange variety (2:3) from warm solutions. Both salts yield the yellow acid on acidifying. The corresponding amide, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CO}\cdot\text{NH}_2$, obtained by condensing *p*-nitro-*o*-toluamide with anisaldehyde, has m. p. 255°.

2-Nitro-4-cyano-4'-acetoxystilbene, from *o*-nitro-*p*-toluonitrile and *p*-hydroxybenzaldehyde followed by acetylation of the resinous product, has m. p. 186°. 4-Nitro-2-cyano-4'-hydroxystilbene forms golden-yellow needles, m. p. 226°, and yields an acetate, m. p. 176°. 2-Nitro-4'-dimethylaminostilbene-4-carboxylic acid, from the nitrile (*ibid.*), crystallises in almost black, broad, flat needles, m. p. 263°, which yield a yellow hydrochloride and a dark red potassium salt.

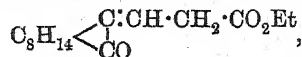
J. C. W.

β -Camphorylidenepropionic Acid (Methylenecamphor-acetic Acid). H. RUPE and E. BURCKHARDT (*Ber.*, 1916, 49, 2547—2563).—It was recently shown that chloromethylenecamphor is a reactive substance capable of giving rise to many camphor derivatives, and several alkyl and alkylidene compounds were then described (*A.*, 1916, i, 409). An attempt has now been made to condense the substance with ethyl sodioacetoacetate in order to obtain ultimately a diketone, thus:



The product obtained, however, is ethyl β -camphorylidenepropionate, which suggests that the intermediate acetoacetate is so unstable that alcoholysis takes place, and the acetyl group is eliminated as ethyl acetate. The properties and reactions of the new ester and the corresponding acid form the subject of the present paper.

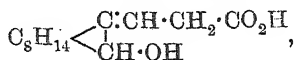
A solution of sodium ethoxide is gradually added to a well-stirred mixture of chloromethylenecamphor and ethyl acetoacetate at 60°, and then, after heating for a further hour or two and removing the alcohol, the residue is just acidified and extracted with ether. On distillation (12 mm.), ethyl acetate, ethyl acetoacetate, chloromethylenecamphor, and ethoxymethylenecamphor are collected in small quantities in the order named, and then the main fraction, ethyl β -camphorylidenepropionate,



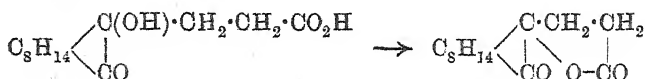
is obtained as a fairly viscous, highly refractive oil, b. p.

173—174°/12 mm., or 291°/737 mm. (slight decomposition), D_4^{20} 1.0417, the yield being about 70%. The residue crystallises in slender, yellow needles, m. p. 265—267°, and is apparently $\alpha\gamma$ -dicamphorylidene propane, $\text{CH}_2(\text{CH}:\text{C}_{10}\text{H}_{14}\text{O})_2$.

β -Camphorylidene propionic acid is obtained after hydrolysing the ester with cold, concentrated hydrochloric acid, in well-developed, rhombic crystals ($a:b:c=0.6414:1:1.2472$), m. p. 106°. It absorbs bromine, is oxidised by ozone to camphorquinone, and is reduced by sodium amalgam to a borneol derivative,

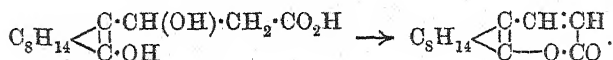


white leaflets, m. p. 51—52°, b. p. 196—198°/13 mm., which will be investigated more fully. The failure to saturate the ethylene linking in the $\beta\gamma$ -position is, of course, quite normal, but an attempt was made to saturate the chain by first displacing this linking into the $\alpha\beta$ -position. When, however, for this purpose, the acid (or ester) is boiled or shaken with concentrated potassium hydroxide, the elements of water are first attached, and the product is the lactone of the β -hydroxycamphorylpropionic acid so formed, thus:



The lactone has m. p. 207° (decomp.), and is oxidised by ozone to a substance, m. p. 210—211°, soluble in sodium carbonate, but not to camphorquinone. The silver and barium salts of the hydroxy-acid are described.

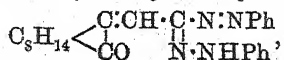
If the ester or acid is dissolved in concentrated sulphuric acid, it is supposed that the elements of water are again attached, that a δ -lactone is produced with the camphor residue in the enolic form, and more water eliminated, thus:



The lactone which results crystallises in long, silky needles, m. p. 66°, b. p. 162—163°/10 mm., has a penetrating odour, absorbs bromine, forming a compound, $\text{C}_{13}\text{H}_{15}\text{O}_3\text{Br}$ (scales, m. p. 104—105°), and does not yield camphorquinone on treatment with ozone.

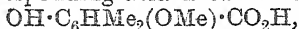
The acid readily loses carbon dioxide on heating at 160°, yielding ethylidenecamphor, b. p. 101—102°/10 mm., m. p. 20—22°, $[\alpha]_D +203.4^\circ$ (*ibid.*).

The acid also reacts with diazonium salts in alkaline solutions, being in this respect also analogous to β -benzylidenepropionic acid, but the products have much greater tinctorial properties. Benzene-diazonium chloride yields "*formazyl methylenecamphor*,"



as a red powder, m. p. 152—154°, and diazobenzenesulphonic acid gives a dye which colours silk pale wine-red and wool "tango" shades.
J. C. W.

Lichen Products. II. Synthesis of Rhizonic Acid.
ADOLF SONN (*Ber.*, 1916, **49**, 2589—2593).—2:6-Dinitro-*p*-xylene (A., 1916, i, 391) is converted into 2-nitro-*p*-xylen-6-ol (Kostanecki, 1886), and this is methylated by means of methyl sulphate. The 2-nitro-6-methoxy-*p*-xylene, very long, stout needles, m. p. 62—62·5°, is then reduced to the hydrochloride of the base, $C_8H_{13}ON, HCl, H_2O$, long, silky needles, m. p. 250—251° (decomp.), and this is converted into the monomethyl ether of β -orcinol. This is transformed into 1-hydroxy-6-methoxy-5-aldehydo-*p*-xylene by means of anhydrous hydrogen cyanide and hydrogen chloride in the presence of aluminium chloride (glistening, thin prisms, m. p. 136°), and when this aldehyde is acetylated, oxidised, and hydrolysed again, the corresponding acid is obtained,



which proves to be identical with naturally occurring rhizonic acid.
J. C. W.

Crystallographical and Optical Observations on some Organic Compounds. G. AMINOFF (*Arkiv Kem. Min. Geol.*, 1916, **6**, No. 4, 1—15).—Details are given in connexion with the crystallographical and optical constants of the following compounds: acetophenone, chloroacetophenone, bromoacetophenone, benzoylacetiminoethyl ether [$COPh \cdot CH_2 \cdot C(NH) \cdot OEt$], and cyanoacetophenone. The morphological relation between the first four substances is shown by their axial ratios ($a:b:c$), which are respectively: 1·0428:1:?, $\beta = 111^\circ 10'$, 0·9957:1:0·4270, 0·9713:1:0·4348, and 1·2962:1:0·5962. Acetophenone is monoclinic, whereas the other three substances belong to the rhombic system. Cyanoacetophenone is probably monoclinic, but well-developed crystals could not be obtained.
T. S. P.

Action of an Alcoholic Solution of Potassium Hydroxide on Ketones. IV. Action of Alcoholic Potassium Hydroxide Solution on Halogeno-aminobenzophenones. P. J. MONTAGNE (*Rec. trav. chim.*, 1917, **36**, 258—270. Compare A., 1908, i, 988; 1913, i, 55; this vol., i, 35).—A continuation of the study of the influence of substituents on the reduction of benzophenone to benzhydrols by alcoholic potassium hydroxide. A single amino-group in the meta-position hinders, although to a less extent than two amino-groups in the meta-positions, the reducing action of alcoholic potassium hydroxide. The introduction of one or more halogen atoms in the para-position is sufficient to neutralise this influence. A number of such halogenated compounds, namely, 4-chloro-, 4-bromo-, 4'-chloro-, 4'-bromo-, 4:4'-dichloro-, and 4:4'-dibromo-3-aminobenzophenones, have been prepared and studied. In the case of the 4-chloro- and 4:4'-dichloro-3-aminobenzophenones, there was only slight replacement of the halogen during the reaction, but with

the others the replacement was more marked. Except in the case of 4-chloro-3-aminobenzhydrol, alcoholic potassium hydroxide causes a more or less marked displacement of the halogen in the halogenated -3-aminobenzhydrols.

The following new compounds are described: 4-chloro-3-aminobenzhydrol, needles, m. p. $74\cdot75^{\circ}$ (corr.); 4-bromo-3-aminobenzophenone, from the corresponding nitro-compound, crystallises in monoclinic prisms [F. M. JAEGER, $a:b:c=1\cdot9883:1:1\cdot1745$; $\beta=86^{\circ}58'$], b. p. $254\cdot5^{\circ}/17$ mm., m. p. 85° (corr.), and yields 4-bromo-3-aminobenzhydrol, needles, m. p. $78\cdot5^{\circ}$ (corr.); 4'-bromo-3-aminobenzophenone, m. p. 135° (corr), b. p. $250^{\circ}/11$ mm., yields 4'-bromo-3-aminobenzhydrol, m. p. $87\cdot25^{\circ}$ (corr.); 4:4'-dibromo-3-aminobenzophenone has m. p. $149\cdot75^{\circ}$ (corr.), and gives 4:4'-dibromo-3-aminobenzhydrol, m. p. $116\cdot75^{\circ}$ (corr.).

4'-Chloro-3-aminobenzophenone, b. p. $235-237^{\circ}/10$ mm., m. p. $116\cdot5^{\circ}$ (corr.), gives 4'-chloro-3-aminobenzhydrol, m. p. 92° (corr.); 4:4'-dichloro-3-aminobenzophenone (compare Montagne, A., 1902, i, 472) yields 4:4'-dichloro-3-aminobenzhydrol, m. p. 94° (corr.).

W. G.

Condensation of Acetone with Imines. CHARLES MAYER (*Bull. Soc. chim.*, 1916, [iv], 19, 452-456. Compare A., 1905, i, 214, 357, 429).—The three benzylidenetoluidines do not behave like benzylideneaniline when mixed in cold alcoholic solution with acetone. Benzylidene-*o*-toluidine does not react. Benzylidene-*m*-toluidine gives a compound, $C_{24}H_{23}ON$, white crystals, m. p. 181° , which, from the fact that it does not reduce a cold acetone solution of potassium permanganate, does not condense with phenylcarbimide and is not decomposed by piperidine, the author considers to be 2:6-diphenyl-1-*m*-tolylpiperid-4-one. Benzylidene-*p*-toluidine under the above conditions, gives, with acetone, β -*p*-toluidino- β -phenylethyl styryl ketone,

$C_7H_7\cdot NH\cdot CHPh\cdot CH_2\cdot CO\cdot CH\cdot CHPh$,
pale yellow crystals, m. p. 138° , which readily reduces potassium permanganate, gives phenyl-*p*-tolylcarbamide, prismatic needles, m. p. 226° , with phenylcarbimide, and is decomposed in boiling alcoholic solution by a few drops of piperidine, giving distyryl ketone and *p*-toluidine. Piperonylideneaniline at the end of several months gives, with acetone in alcoholic solution, a compound, felted, yellow needles, m. p. 188° , which dissolves in sulphuric acid to a magenta solution, the colour disappearing on addition of water, and is not decomposed in boiling alcoholic solution by piperidine. Piperonylideneaniline gives with styryl methyl ketone in alcoholic solution a compound, m. p. 170° , dissolving in sulphuric acid to a reddish-yellow solution, the colour disappearing on the addition of water.

W. G.

The Friedel-Crafts' Reaction. I. Phthalyl Chloride and the Mechanism of its Reaction with Benzene. MAURICE COPISAROW (T., 1917, 111, 10-20).—It is already known that the condensation of phthalyl chloride with benzene in the presence of

aluminium chloride gives rise to diphenylphthalide as main product, with some anthraquinone, *o*-benzoylbenzoic acid, and diphenylanthrone, and that at low temperatures *o*-benzoylbenzoic acid becomes the chief product (Scheiber, A., 1913, i, 976). The author has now discovered the formation also of phenylloxanthranol, and *tetraphenylmethane-o-carboxylic acid*, both of which are also obtainable by the interaction of diphenylphthalide with benzene. These results, together with the work of Ott (A., 1912, i, 828), Scheiber (A., 1913, i, 976), Meyer (A., 1904, i, 747), and Copisarow and Weizmann (A., 1915, i, 687), indicate the condensation to be of complex character due to the tendency of the phthalyl chloride and of its condensation products to assume cyclic structure and to the capacity of the cyclic compounds to undergo further condensation with benzene.

Haller and Guyot (A., 1899, i, 221) attributed the formation of diphenylanthrone to the presence of phthalylene chloride in the phthalyl chloride, but evidence is now adduced to show that all the above-mentioned compounds are produced in the condensation of phthalyl chloride and benzene. The mechanism of the formation of each of the compounds is considered, and equations are given representing the probable reactions in each case with indications of the most favourable conditions.

For experimental details see the original paper.

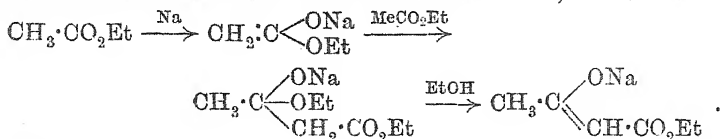
D. F. T.

3:4-Benzofluorenone. PAUL PFEIFFER (*Ber.*, 1916, 49, 2425).—The author obtained a ketone (A., 1907, i, 931) from a polymeride of ethyl phenylpropiolate which he suggested might be *allochrysoketone* (3:4-benzofluorenone). Comparing it with the account of this substance recently given by Schaarschmidt (A., 1916, i, 731), the assumption is found to have been correct. J. C. W.

The Relationships of the Polymeric Ketens to cyclobutane-1:3-dione and its Derivatives. G. SCHROETER [with H. KESSELER, O. LIESCHE, and R. F. MÜLLER (*Ber.*, 1916, 49, 2697—2745)].—Various dimeric ketens have been formulated as derivatives of *cyclobutane-1:3-dione*, and dimeric keten itself is usually regarded as this parent diketone (compare Staudinger, and Chick and Wilsmore, T., 1910, 97, 1978—2000). True derivatives of the *cyclodiketone* have now been prepared, in addition to dimethyl*cyclobutane-2:4-dione* (A., 1907, i, 533), by synthesis from dialkylacetonedicarboxylates, and they are found to differ in important respects from the dimeric ketens. Genuine *cyclobutane-1:3-dione* has not yet been prepared in this way, but the author prophesies that it will prove to be different from dimeric keten. Indeed, Chick and Wilsmore themselves expressed some doubt as to the cyclic nature of this substance (*loc. cit.*, p. 1982). The main differences between dimeric keten and dialkyl*cyclobutane-2:4-diones* are as follows: (i) dimeric keten is a liquid with an unbearable odour; dialkyl*cyclobutanediones* are odourless solids; (ii) dimeric keten gives no simple ketone derivatives; dialkyl*cyclobutanediones* give monophenylhydrazones and dioximes; (iii) dimeric keten forms ethyl acetoacetate when treated with alcohol containing a trace of

sodium ethoxide; the diketones form normal salts in aqueous or alcoholic solutions when treated with metallic oxides or carbonates.

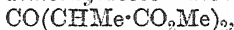
The last-named reaction of a keten offers another explanation of the conversion of ethyl acetate into ethyl acetoacetate, involving the transformation of the ester into a keten form, thus:



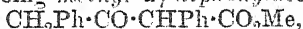
Dimeric ketens can, however, change into true *cyclobutanediones* (see Staudinger, A., 1911, i, 306, etc.), and therefore the chemistry of these substances is complicated by the possibility of depolymerisation, and of internal rearrangement into unimolecular compounds which may be identical with or similar to the genuine *cyclobutanediones* or the products left on the rupture of their rings.

I. *Syntheses of Dialkylacetonedicarboxylates*.—Useful directions for the preparation of methyl and ethyl acetonedicarboxylates and of the free acid from citric acid are given.

The following dialkyl derivatives were obtained from these esters by the action of the alkyl haloids in the presence of sodium methoxide solution: *methyl dimethylacetonedicarboxylate*,

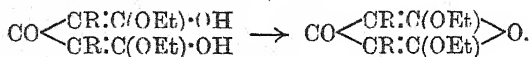


b. p. 125°/9 mm., and the corresponding *ethyl ester*, b. p. 128°/12 mm.; *ethyl diethylacetonedicarboxylate*, b. p. 150°/12 mm.; *ethyl diisopropylacetonedicarboxylate*, b. p. 162°/16 mm.; and *ethyl diallylacetonedicarboxylate*, b. p. 150°/15 mm. A diphenylacetonedicarboxylate could not be obtained in this way, and therefore an attempt was made to synthesise one by the action of methyl carbonate on dibenzyl ketone in the presence of sodium suspended in ether. In this reaction, however, the synthesis stops at the first phase, the product being *methyl α-diphenylacetoacetate*,



which crystallises in long needles, m. p. 59—60°. This may also be prepared by the action of sodium methoxide on methyl phenylacetate, and it yields 1:3-dihydroxy-2-phenylnaphthalene when dissolved in concentrated sulphuric acid (compare Volhard, A., 1897, i, 423).

II. *Condensation of the Dialkylacetonedicarboxylates to Dialkylcyclobutanedionedicarboxylates and Dialkylxydialkylpyrones*.—When the above esters are carefully stirred into cold sulphuric acid monohydrate they yield the acidic diketones and feebly basic pyrones as by-products. The latter are produced by the elimination of water from ketenoid forms of the esters, thus:



Methyl dimethylacetonedicarboxylate yields *methyl 1:3-dimethylcyclobutane-2:4-dione-1-carboxylate*, $\text{CHMe} \begin{array}{l} \text{O} \\ \text{CO} \end{array} \text{CMe} \cdot \text{CO}_2 \text{Me}$, m. p. 156—157°, and *2:6-dimethoxy-3:5-dimethyl-1:4-pyrone*, in

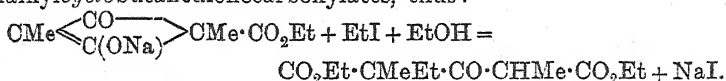
bundles of large prisms, m. p. 165°. If fuming sulphuric acid is used (13% SO_3) an unstable compound, $\text{CO}_2\text{Me}\cdot\text{CHMe}\cdot\text{C}\begin{smallmatrix} \text{O}\cdot\text{SO}_2\cdot\text{O} \\ \text{CMe}\cdot\text{CO} \end{smallmatrix}$, m. p. 67—68°, is formed as well.

Diethyl dimethylacetonedicarboxylate gives *ethyl 1:3-dimethylcyclobutane-2:4-dione-1-carboxylate*, m. p. 133—135° (compare A., 1907, i, 533), and *2:6-diethoxy-3:5-dimethyl-1:4-pyrone*, m. p. 87—88°. *Ethyl 1:3-diethylcyclobutane-2:4-dionecarboxylate* forms long needles, m. p. 101·5—102·5°, and the *methyl ester* has m. p. 113·5—116°. The latter was prepared from a crude methyl diethylacetonedicarboxylate, b. p. 140—144°/12 mm., obtained by oxidising methyl β -hydroxy- $\alpha\alpha$ -diethylglutarate, b. p. 143°/16 mm., with chromic acid, this ester being produced by the interaction of zinc, methyl α -bromobutyrate, and methyl formate.

Ethyl diallylacetonedicarboxylate yields *ethyl 1:3-diallylcyclobutane-2:4-dione-1-carboxylate*, m. p. 105—107·5°.

III. Transformations and Rupture of the Ring in the Series of *Dialkylcyclobutanedionecarboxylates*.—When boiled with water, methyl dimethylcyclobutanedionecarboxylate loses carbon dioxide and changes into *methyl β -keto- α -methylvalerate*, b. p. 80°/12 mm., which condenses with phenylhydrazine to form *1-phenyl-4-methyl-3-ethylpyrazole-5-one*, $\text{CO}\begin{smallmatrix} \text{NPh}-\text{N} \\ \text{CHMe}\cdot\text{CEt} \end{smallmatrix}$, m. p. 111·5°.

Trialkylacetonedicarboxylates are formed when the alkyl haloids are boiled with alcoholic solutions of the sodium salts of the dialkylcyclobutanedionecarboxylates, thus:



Ethyl δ -methylhexan- γ -one- $\beta\delta$ -dicarboxylate has b. p. 150°/15 mm.; *ethyl δ -benzylpentan- γ -one- $\beta\delta$ -dicarboxylate* has b. p. 195—196°/14 mm.; *ethyl ϵ -ethylheptan- δ -one- $\gamma\epsilon$ -dicarboxylate* has b. p. 163°/13 mm.; *ethyl ϵ -methylheptan- δ -one- $\gamma\epsilon$ -dicarboxylate* has b. p. 152°/15 mm.; and *ethyl ϵ -benzylheptan- δ -one- $\gamma\epsilon$ -dicarboxylate* has b. p. 206—207°/15 mm.

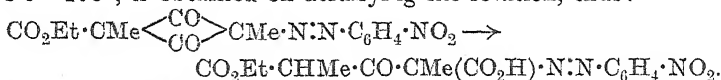
Ethyl dimethylcyclobutanedionecarboxylate reacts with pure hydrazine hydrate to form *4-methylpyrazole-5-one-3- α -propionhydrazide*, $\text{CO}\begin{smallmatrix} \text{NH}-\text{N} \\ \text{CHMe}\cdot\text{C}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2 \end{smallmatrix}$, m. p. 212—213°, but with dilute methyl-alcoholic hydrazine hydrate to form the *azine*, $\left(\text{CO}_2\text{Et}\begin{smallmatrix} \text{CHMe} \\ \text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CHMe} \end{smallmatrix}\text{C}\right)_2\text{N}_2$, in long needles, m. p. 134°.

Methyl dimethylcyclobutanedionecarboxylate reacts with aqueous hydroxylamine to form *4-methylisooxazole-5-one-3- α -propionhydrazamic acid*, $\text{CO}\begin{smallmatrix} \text{O}-\text{N} \\ \text{CHMe}\cdot\text{C}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH} \end{smallmatrix}$ in rosettes of prisms, with $1\text{H}_2\text{O}$, m. p. 152—153° (decomp.).

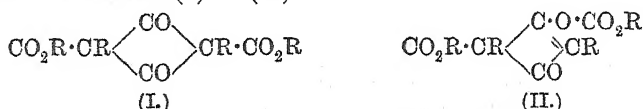
Ethyl diethylcyclobutanedionecarboxylate is converted by warming with aniline into *ethyl heptan- δ -one- $\gamma\epsilon$ -dicarboxanilide*, $\text{CO}_2\text{Et}\cdot\text{CHEt}\cdot\text{CO}\cdot\text{CHEt}\cdot\text{CO}\cdot\text{NHPh}$, needles, m. p. 83°.

Ethyl diethylcyclobutanedionecarboxylate decomposes on distillation in a high vacuum, into ethyl diethylacetonedicarboxylate and an equal weight of a non-volatile resin.

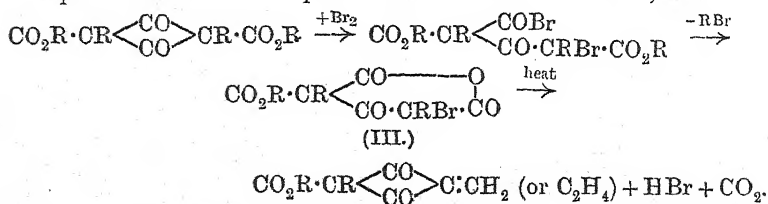
When *p*-nitrobenzenediazonium acetate solution is added to a cold alkaline solution of ethyl dimethylcyclobutanedionecarboxylate the *p*-nitrobenzeneazo-compound is precipitated, m. p. 152—153·5°; this dissolves in sodium hydroxide with a deep red colour, but *ethyl hydrogen p*-nitrobenzeneazodimethylacetonedicarboxylate, m. p. 195·5—196°, is obtained on acidifying the solution, thus:



Further experiments had for their object the introduction of a second carboxyl group into the cyclobutanediones. This is achieved by the action of ethyl chloroformate on the sodium salts, suspended in toluene and just sufficient alcohol, or on the esters dissolved in pyridine. It is found that the esters do not react with sodium in benzene or toluene solutions, which suggests that in the free state they are true diketones, and not keto-enols, as used to be supposed. The sodium salt of ethyl dimethylcyclobutanedionecarboxylate is a white powder. *Ethyl diethylcyclobutanedionedicarboxylate* has b. p. 162—163°/1 mm., and yields ethyl diethylcyclobutanedionecarboxylate when left with sodium ethoxide solution. *Methyl dimethylcyclobutanedionedicarboxylate* crystallises in felted needles or stout prisms, m. p. 52—53°, b. p. 130°/0·2 mm. This solid ester, and to a lesser extent the oily ethyl ester, are remarkably stable towards water, for scission of the ring only takes place slowly even on heating. Some doubt might exist as to whether these esters conform to formula (I) or (II):

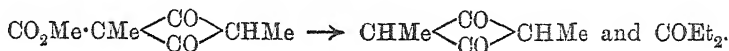


To decide this question, the esters were treated with bromine in the expectation that absorption would take place or not, as the case might be. The reaction is very complex, however, for an atom of bromine is found to enter the molecule and alkyl to be eliminated from a carboxyl group as alkyl bromide. The products lose carbon dioxide and hydrogen bromide on heating, and the whole process is explained on the assumption that formula I is correct, thus:



The methyl compound conforming to III has m. p. 158—160°, the ethyl compound, m. p. 41·5—42·5°.

IV. *Degradation of the Dialkylcyclobutanedionecarboxylates to Dialkylcyclobutanediones.* When methyl dimethylcyclobutanedionecarboxylate is heated with milk of baryta, some diethyl ketone passes away in the steam, and the barium salt of dimethylcyclobutane-1:3-dione remains in the solution, both "ketone" and "acid" hydrolysis taking place, thus:

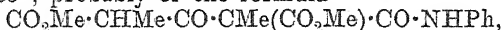


The diketone has been briefly described already (A., 1907, i, 533). It decomposes silver carbonate, but when the silver salt is treated with hydrogen sulphide in ethereal suspension, no desmotropic form of the diketone is produced. The enolic form seems to be incapable of separate existence. Dimethylcyclobutane-1:3-dione also forms a *phenylhydrazone*, $\text{C}_6\text{H}_5\text{O:N}\cdot\text{NHPh}$, yellow needles, m. p. 160°, and a *dioxime*, m. p. 196—198° (decomp.), and it may be produced, although not readily, by Staudinger's method from α -bromopropionyl bromide through methylketen. *Diethylcyclobutane-1:3-dione*, prepared in the same way from ethyl diethylcyclobutanedionecarboxylate, has m. p. 76—78°, forms a *silver salt*, $\text{C}_8\text{H}_{11}\text{O}_2\text{Ag}$, white leaflets, and a *phenylhydrazone*, m. p. 132.5—133.5°.

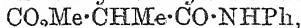
V. *Comparison of Dimeric Ketens with the Synthetic cyclobutanedione Derivatives.*—The main purpose of this section of the paper is to show that dimeric ketencarboxylic esters are depolymerised and then combine with the elements of alcohol when a small shaving of sodium is added to the alcoholic solutions. The dimeric ketens are mostly obtained by heating aliphatic diazo-compounds in xylene or amyl ether (compare Staudinger, A., 1916, i, 847—856). For example, *dimeric methyl methylketencarboxylate*,



m. p. 94—96°, from methyl diazoacetoacetate, yields methyl methylmalonate. It also combines with aniline, forming a *compound*, m. p. 83—85°, probably of the formula



and not identical with *methyl methylmalonanilate*,



m. p. 83—86°, for a mixture of these has m. p. 65—75°. Similarly, the brown oil left after heating ethyl diazobenzoylacetate with xylene can be converted into ethyl phenylmalonate, and dimeric keten itself into methyl or ethyl acetoacetate according to the alcohol chosen.

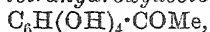
The decomposition of diazodiacetylmethane, diazobenzoylacetylmethane, diazoacetone, and diazoacetophenone was also studied, but no indications of the presence of mono- or di-meric ketens or cyclobutanedione derivatives in the products could be obtained.

J. C. W.

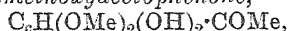
Synthesis of Hydroxyquercetin. MAXIMILIAN NIERENSTEIN (T., 1917, 111, 4—10).—A description of the synthesis of hydroxyquercetin (Nierenstein and Wheldale, A., 1912, i, 42) on the lines

of that of quercetin (Kostanecki, Lampe, and Tambor, A., 1904, i, 517).

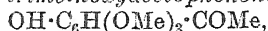
1:2:3:5-Tetrahydroxybenzene (phentetrol), prepared by a convenient modification of Oettinger's method (A., 1895, i, 457), was converted into 2:3:4:6-tetrahydroxyacetophenone,



by heating with acetic acid in the presence of zinc chloride; this product, by treatment with methyl sulphate, gave, successively, 2:6-dihydroxy-3:4-dimethoxyacetophenone,



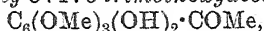
and 2-hydroxy-3:4:6-trimethoxyacetophenone,



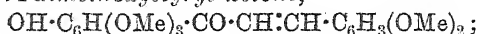
together with smaller quantities of tetramethoxyacetophenone, $\text{C}_6\text{H}(\text{OMe})_4 \cdot \text{COMe}$, and 6-hydroxy-2:3:4-trimethoxyacetophenone.

2-Hydroxy-3:4:6-trimethoxyacetophenone, of which the constitution was confirmed by oxidation to 3:4:6-trimethoxy-2:5-quinacetophenone, $\text{OMe} \cdot \text{C} \begin{smallmatrix} \text{C}(\text{OMe}) \cdot \text{C} \\ \text{CO} \cdot \text{C}(\text{OMe}) \end{smallmatrix} \cdot \text{C} \cdot \text{COMe}$, and conversion of

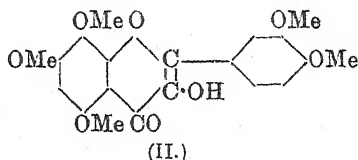
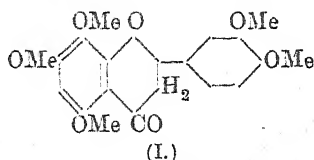
this into 2:5-dihydroxy-3:4:6-trimethoxyacetophenone,



by heating with zinc dust and acetic anhydride, followed by hydrolysis, was made to undergo condensation with veratraldehyde in the presence of alkali, with formation of 2-hydroxy-3:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone,



this substance, when heated with hydrochloric acid, underwent intramolecular condensation to 5:7:8:3':4'-pentamethoxyflavanone (I), which was then successively converted into 3-oximino-5:7:8:3':4'-pentamethoxyflavanone, $\text{C}_{20}\text{H}_{21}\text{O}_8\text{N}$, and



5:7:8:3':4'-pentamethoxyflavonol (II). Demethylation of the last substance by heating with hydriodic acid yielded a product identical with the hydroxyquercetin already described (*loc. cit.*), the formula for hydroxyquercetin being thus shown to be that given in formula II with hydroxyl substituted throughout for methoxyl.

1:2:3:5-Tetrahydroxybenzene was also submitted to the action of potassium hydrogen carbonate in an atmosphere of carbon dioxide (compare Clibbens and Nierenstein, A., 1915, i, 1062), with formation of 2:3:4:6-tetrahydroxybenzoic acid; the tetra-acetyl-, tetrabenzoyl-, and tetramethoxy-derivatives of this acid were prepared, as also were the methyl ester and acid chloride of the tetramethoxy-acid.

For details the original paper should be consulted. D. F. T.

Oxidation of Camphenilone. S. S. NAMETKIN, (MLLE.) E. A. GREKOVA, and (MLLE.) A. M. CHUCHRIKOVA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 453—455).—Camphenilone exhibits marked stability towards oxidising agents, the only definite oxidation product yet obtained being oxalic acid. When heated with dilute nitric acid in a sealed tube, fenchone is converted into secondary and tertiary nitro-derivatives (compare Kononov, A., 1904, i, 257). The authors find that, when camphenilone is heated with nitric acid (D 1·1) in a sealed tube at 140—145°, the products consist of: (1) crystals, m. p. 90—92°, (2) an oil, and (3) *iso*-camphoronic acid. Compounds (1) and (2) are formed in very small proportions, and are probably tertiary nitroketones, two isomerides being possible in this case. The formation of *iso*-camphoronic acid is in complete accord with the accepted formula for camphenilone, and it is probable that the first phase of the oxidation yields α -nitroketone, which then undergoes hydrolysis, and subsequently further oxidation. T. H. P.

Composition of Crude Menthyl Chloride. N. I. KURSANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 867—879).—By the action of phosphorus pentachloride on menthol, Berkenheim (A., 1892, 866) prepared an optically inactive menthyl chloride which, when heated with potassium acetate and acetic acid, is partly converted into menthene and partly remains unchanged; the unchanged portion being *lævorotatory*, the other portion must be *dextrorotatory*. The various samples of menthyl chloride obtained by the author with the help of phosphorus pentachloride or by heating menthol with hydrochloric acid are *lævorotatory* in all cases, the magnitude of the rotation varying within wide limits, but being always less than that of the constant menthyl chloride; besides the latter, these samples may contain, therefore, either an inactive chloride or one with a low *lævorotation*.

In order to throw light on the composition of crude menthyl chloride, the author has investigated two different preparations, both obtained by the action of phosphorus pentachloride on menthol in light petroleum and having (1) b. p. 90—95°/16 mm., $\alpha_D = -10\cdot68^\circ$ in a 20 cm. tube, and (2) b. p. 91—96°/16 mm., $\alpha_D = -14\cdot50^\circ$ in a 20 cm. tube. Each of these samples was repeatedly heated with alcoholic potassium hydroxide, the volatile products being removed after each treatment and the undecomposed menthyl chloride again heated with the alcoholic alkali. The rotations of the different fractions of the crude menthyl chloride decomposed in this way are calculated on the supposition that the rotation of a mixture of menthyl chlorides is an additive magnitude; the accuracy of this supposition is shown by actual experiment. The rotation for the successive fractions at first increases and then diminishes, and in the second case actually changes its sign from positive to negative.

Since it is found that the constant menthyl chloride, even when mixed with those obtained by the combination of menthene with

hydrogen chloride, is not decomposed on heating with alcoholic potassium hydroxide, the results of the experiments on fractional hydrolysis of the crude menthyl chloride are explainable on the assumption that the latter contains the constant menthyl chloride, two unstable, secondary, stereoisomeric chlorides with rotations of opposite sign, and an optically inactive tertiary chloride. The view expressed by various authors (compare Kursanov, A., 1915, i, 420) that crude menthyl chloride consists of a mixture of one tertiary and only two secondary chlorides must, therefore, be regarded as erroneous. From the numerical results of the experiments on fractional hydrolysis, the proportions of constant menthyl chloride in the two samples examined are calculated to be 47·31% and 44·44% respectively.

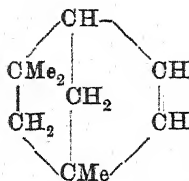
The stereoisomeric relations of these compounds are discussed, and it is shown that the supposition that, in the process of isomerisation of menthol on its conversion into chloride, a part is played by Δ^3 -menthene, explains the occurrence of all the spacial and structural isomerides proved or assumed to be present in crude menthyl chloride; this explanation is therefore regarded as probable.

T. H. P.

Fenchylene, a New Synthetic Terpene. S. S. NAMETKIN and (MLLE.) A. K. RUSHENCEVA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 450—452).—None of the unsaturated hydrocarbons (fenchenes) yet obtained from the near derivatives of fenchane contain the unaltered bicyclic system of fenchane. If Semmler's configuration for fenchane is accepted, it is clear that such hydrocarbons cannot theoretically be derived from fenchyl alcohol. From *isofenchyl* alcohol, such compounds are, however, derivable, and for the terpenes which retain the original fenchane ring-system and thus differ from the fenchenes, the name "fenchylenes" is suggested. The action of zinc chloride on *isofenchyl* alcohol (compare Bertram and Helle, A., 1900, i, 398) yields *Dd*-fenchene (compare Wallach, A., 1908, i, 809), the dehydration being accompanied by profound isomerisation. In order to avoid such isomeric change, the authors have effected the removal of the elements of water from *isofenchyl* alcohol by Tschugaev's xanthate method (A., 1904, i, 327).

Methyl isofenchylxanthate was obtained as a viscous, yellow oil. About one-third of this ester withstands a temperature of 230°, but the remainder decomposes readily at 170—180°, yielding the *fenchylene* (annexed formula), which is a volatile liquid with a faint but characteristic odour recalling that of fenchene, b. p. 139—140°/760 mm., D_D^{20} 0·8381, n_D^{20} 1·4494, $[\alpha]_D - 68·76^\circ$ (in alcohol). With bromine the hydrocarbon unites energetically, and it yields a crystalline *nitrosochloride*, $C_{10}H_8NOCl$, m. p. 131°. Oxidation of fenchylene by means of alkaline permanganate gives *cis*-fenchocamphoric acid (compare A., 1916, i, 269) in 77% yield.

T. H. P.



Adsorption of Alkannin in Different Solvents. M. A. RAKUZIN and (MLLE.) G. F. PEKARSKAJA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 716—718).—A solution of alkannin (anchusic acid) in light petroleum is completely decolorised by animal charcoal, the adsorption being irreversible; similar results are obtained with solutions of the ammonium and sodium salts. In aniline solution, either cold or hot, alkannin is not adsorbed, even by animal charcoal, and when the specific gravity and viscosity of the liquid are lowered by addition of ether, decolorisation is incomplete, only that part of the alkannin dissolved in the ether being adsorbed.

T. H. P.

The Pigments of Molasses and De-saccharification Residues. II. H. STOLZENBERG (*Ber.*, 1916, **49**, 2675—2677. Compare A., 1916, i, 829).—The residue left after separating the pigment contains a considerable quantity of an acid, $C_{34}H_{40}O_{15}N_2$, which is a very bitter, hard, black wax, to which the adhesive properties of molasses are largely due. This may be isolated after removing substances which can be benzoylated, as, for example, the remainder of the pigment.

J. C. W.

The Chemical Constituents of Bituminous Tar Oils Rich in Sulphur (Ichthyol Oils). II. HELMUTH SCHEIBLER (*Ber.*, 1916, **49**, 2595—2600. Compare A., 1916, i, 65).—The author comments on the interesting connexion between his conclusions that the ichthyol oils contain thiophen derivatives and Friedmann's recent discoveries that such compounds can be obtained by the action of sulphur on straight-chain hydrocarbons (A., 1916, i, 735). The association of free sulphur and hydrogen sulphide with asphalt and ichthyol-shale deposits is quite common.

It is suggested that the constitution of thiophens may be elucidated by taking advantage of the fact that potassium attacks them on heating, forming potassium sulphide and an organo-potassium compound which may be converted into an unsaturated acid.

J. C. W.

Sulphides with Four-membered Rings. E. GRISCHKEVITSCH-TROCHIMOVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 880—901).—The action of sodium sulphide on $\alpha\gamma$ -dibromopropane, $\alpha\gamma$ -dibromobutane, and $\beta\delta$ -dibromopentane gives rise to the formation of cyclic sulphides with four-membered rings, but the yields of these compounds are very small. In their chemical characters, such sulphides resemble those of the aliphatic series.

Trimethylene sulphide, $CH_2<\overset{CH_2}{\underset{CH_2}{}}>S$, obtained from $\alpha\gamma$ -dibromopropane and sodium sulphide, is a colourless, highly mobile liquid with an unpleasant, penetrating odour, b. p. $93.8-94.2^\circ/752$ mm., D_4^{25} 1.0284, n_D^{25} 1.5059. It is accompanied by the polymeride, m. p. about 85° , obtained by Mansfeld (A., 1886, 525; 1887, 122) and by Autenrieth and Wolff (A., 1899, i, 579). With mercuric chloride it forms a white, microcrystalline compound, $C_3H_6S.HgCl_2$, which begins to contract at about $93-95^\circ$ and then decomposes without melting. It yields a *methiodide*, $C_3H_6S.2MeI$, which forms colour-

less needles, m. p. 98·5—99°, and probably has the structure $C_3H_6 \cdot SMe_2I_2$, the two atoms of iodine being precipitable by means of silver nitrate. When oxidised by permanganate, trimethylene sulphide yields *trimethylenesulphone*, $CH_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} SO_2$, which crystallises in needles, m. p. 75·5—76°. The action of alcoholic ammonia on trimethylene sulphide in a sealed tube at 200° gives *γ-aminopropyl mercaptan*, $NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot SH$, which yields a *platinichloride*, $(C_3H_9NS)_2 \cdot H_2PtCl_6$, the latter forming a pale orange powder decomposing without melting at 155—160°. Attempts to convert trimethylene sulphide into (1) the alcoholic mercaptan, $OH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot SH$, by the action of water, and (2) trimethylene oxide by the action of silver oxide, were unsuccessful.

For the preparation of allylcarbinol, conditions have been found which give yields almost double those obtained by Pariselle (A., 1909, i, 282; 1910, i, 353); the product obtained by the author has b. p. 112·5—113·5° (corr.)/755 mm., $D_4^{17.5}$ 0·8379, $n_D^{17.5}$ 1·4146. The *phenylurethane*, $C_{11}H_{13}O_2N$, forms colourless needles, m. p. 23·5—24·5°.

2-Methyltrimethylene sulphide, $CH_2 \begin{smallmatrix} \text{CHMe} \\ \text{CH}_2 \end{smallmatrix} S$, obtained from *αγ*-dibromobutane, is a colourless, highly mobile liquid with an unpleasant odour, b. p. 105·5—107·5° (corr.)/747 mm., D_4^{20} 0·9571, n_D^{20} 1·4831; it is accompanied by the polymeric sulphide, which is a yellow, amorphous powder, and by the halogenated thio-ether (?). It forms a *methiodide*, $C_4H_9S \cdot 2MeI$, which crystallises in colourless needles, m. p. 123—124°, and an additive *mercuric chloride* compound, $C_4H_9S \cdot HgCl_2$, which begins to contract at 103—104° and at a higher temperature decomposes without melting. When oxidised with permanganate, it gives *2-methyltrimethylenesulphone*, $CH_2 \begin{smallmatrix} \text{CHMe} \\ \text{CH}_2 \end{smallmatrix} SO_2$, which is a colourless, viscous, almost odourless liquid with a bitter taste, b. p. 251·5—253·5° (corr.), $D_4^{16.5}$ 1·2174, $n_D^{16.5}$ 1·4700.

2:4-Dimethyltrimethylene sulphide, $CH_2 \begin{smallmatrix} \text{CHMe} \\ \text{CHMe} \end{smallmatrix} S$, obtained from *βδ*-dibromopentane, is a colourless, highly mobile liquid with a faintly terpenic odour, b. p. 112·5—113·5° (corr.)/757 mm., D_4^{18} 0·8710, n_D^{18} 1·4502. With mercuric chloride it forms a *compound*, $C_5H_{10}S \cdot HgCl_2$, m. p. 90—91°, and oxidation with permanganate converts it into *2:4-dimethyltrimethylenesulphone*, $C_5H_{10} \cdot SO_2$, which is a colourless, viscous liquid, b. p. 255—255·5° (corr.)/758 mm., $D_4^{17.5}$ 1·1589, $n_D^{17.5}$ 1·4653. T. H. P.

Sulphides with Five-membered Rings. E. GRISCHKEVITSCH-TROCHIMOVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 901—928).—Tetrahydrothiophen (compare von Braun and Trümpler, A., 1910, i, 274), prepared by the action of sodium sulphide on *αδ*-dibromobutane or *αδ*-di-iodobutane (compare Hamonet, A., 1901, i, 247), is a colourless, mobile liquid with an intense odour, b. p. 118—119°, D_4^{19} 0·9607, n_D^{19} 1·4871. With mercuric chloride it forms the *com-*

pound, $C_4H_9S, HgCl_2$, which crystallises in long, slender needles, m. p. $124.5-125.5^\circ$, and, when oxidised with permanganate, it yields the corresponding *sulphone*, $\begin{matrix} CH_2 \cdot CH_2 \\ | \quad | \\ CH_2 \cdot CH_2 \end{matrix} > SO_2$, which forms an almost odourless, viscous, bitter liquid, b. p. $285-288^\circ$ (corr.)/743 mm., $153-154^\circ$ (corr.)/18 mm., $D_4^{18.2} 1.2723$, $n_D^{18.2} 1.4833$, or long needles, m. p. $8-10^\circ$, and exhibits normal cryoscopic behaviour in water. When distilled through a glass tube at a dull red heat, tetrahydrothiophen undergoes partial conversion into thiophen.

[With L. NEKRITSCH.]—2-Methyltetrahydrothiophen (compare von Braun, A., 1911, i, 75), obtained by the action of sodium sulphide on $\alpha\delta$ -dibromopentane in aqueous alcoholic solution, is a colourless, mobile liquid with a disagreeable odour, b. p. $132.5-132.6^\circ$ (corr.)/750 mm., $D_4^{18} 0.9564$, $n_D^{18} 1.4886$. With mercuric chloride it forms a *compound* which decomposes, without melting, at about 150° . Its *methiodide*, $C_4H_7Me \cdot SMeI$, forms long, slender, colourless needles, and, in the open, volatilises without melting at $151-152^\circ$, but in a sealed capillary has m. p. 155° (decomp.). When oxidised with dilute nitric acid, 2-methyltetrahydrothiophen yields the *sulphoxide*, $C_4H_7Me \cdot S \cdot O$, which is a viscous, slightly coloured liquid with an unpleasant odour and an intensely bitter taste. Permanganate, however, converts 2-methyltetrahydrothiophen into the *sulphone*, $C_4H_7Me \cdot SO_2$, which is a colourless, viscous liquid, b. p. $279-280^\circ$ (corr.)/758 mm., $D_4^{18} 1.2070$, $n_D^{18} 1.4801$, and has the normal molecular weight in freezing water.

3-Methyltetrahydrothiophen, $\begin{matrix} CHMe \cdot CH_2 \\ | \quad | \\ CH_2 - CH_2 \end{matrix} > S$, obtained by the action of sodium sulphide on $\alpha\delta$ -dibromo- β -methylbutane in alcoholic solution, is a colourless, mobile liquid resembling analogous sulphides in taste and odour, b. p. $137.5-138.5^\circ$ (corr.)/740 mm., $D_4^{18.5} 0.9596$, $n_D^{18.5} 1.4886$. With mercuric chloride it forms a *compound*, $C_5H_{10}S, HgCl_2$, m. p. $82-83^\circ$.

meso-2:5-Dimethyltetrahydrothiophen, $\begin{matrix} CH_2 \cdot CHMe \\ | \quad | \\ CH_2 \cdot CHMe \end{matrix} > S$, obtained by the action of sodium sulphide on the *meso*-form of $\beta\epsilon$ -dibromohexane (compare Wislicenus, A., 1901, i, 664), forms a colourless, mobile liquid of disagreeable odour, b. p. $142-142.2^\circ$ (corr.)/756 mm., $D_4^{18} 0.9391$, $D_4^{21.5} 0.9175$, $D_4^{100} 0.8415$, $n_D^{21.5} 1.4752$. Its *methiodide*, $C_4H_6Me_2 \cdot SMeI$, forms slender needles, volatilising without melting at $156-158^\circ$. On oxidation it gives (1) with dilute nitric acid, the *sulphoxide*, $C_4H_6Me_2 \cdot SO$, which is a viscous, pale yellow liquid with a disagreeable odour, or (2) with permanganate, the *sulphone*, $C_4H_6Me_2 \cdot SO_2$, which is a colourless, almost odourless, viscous liquid, b. p. $277.5-278^\circ$ (corr.)/749 mm., $D_4^{18} 1.1532$, $n_D^{18} 1.4772$, and exhibits normal cryoscopic behaviour in water. The *compound* with mercuric chloride melts at $109-110^\circ$ to a turbid liquid and decomposes on further heating.

[With S. GALPERIN.]—2-Iodo-3:5-dimethylthiophen, $\begin{matrix} CH \cdot CMe \\ | \quad | \\ CMe = CI \end{matrix} > S$,

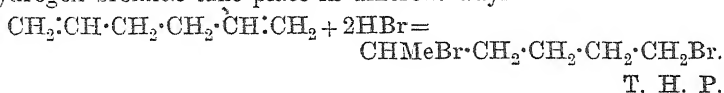
prepared by the action of iodine on 3:5-dimethylthiophen in benzene solution containing mercuric oxide, forms a pale yellow liquid, b. p. 119—120.5°/20 mm., D_4^{20} 1.7474, n_D^{20} 1.6058. From this compound, by way of the organo-magnesium derivative, 3:5-dimethylthiophen-2-carboxylic acid (compare Zelinski, A., 1887, 921; 1888, 939) was prepared. Reduction of the latter by means of sodium amalgam yields 3:5-dimethyltetrahydrothiophen-2-carboxylic acid, $\begin{array}{c} \text{CH}_2\text{---CHMe} \\ \text{CHMe}\cdot\text{CH}(\text{CO}_2\text{H}) \end{array} > \text{S}$, which forms colourless needles, m. p. 98.5—99.5°; its *silver* salt was analysed. T. H. P

Sulphides with Six-membered Rings. E. GRISCHKEVITSCH-TROCHIMOVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 928—943).—[With O. CYKINA.]—Pentamethylene sulphide (compare von Braun and Trümpler, A., 1910, i, 274), obtained in good yield by the action of sodium sulphide on *ae*-dibromopentane, forms a colourless, mobile liquid, resembling other cyclic sulphides in odour, b. p. 141.5—142° (corr.)/747 mm., D_4^{18} 0.9943, n_D^{18} 1.5046; its structure is confirmed by its non-identity with 2:4-dimethyltrimethylene sulphide or with 2- or 3-methyltetrahydrothiophen (see preceding abstracts). It does not undergo isomeric change when heated in a sealed tube at 200°. Its *methiodide*, $\text{C}_5\text{H}_{10}\text{S}\cdot\text{MeI}$, forms thin, colourless needles volatilising, without melting, at 162°, and its *compound* with mercuric chloride, $\text{C}_5\text{H}_{10}\text{S}\cdot\text{HgCl}_2$, shining, silvery plates, m. p. 137.5°, resembling boric acid crystals. In solution in carbon tetrachloride it combines with bromine, giving the highly unstable *dibromide*, $\text{C}_5\text{H}_{10}\text{S}\cdot\text{SBr}_2$. Dilute nitric acid converts it into the *sulphoxide*, $\text{C}_5\text{H}_{10}\text{S}\cdot\text{SO}$, which is obtained as a transparent, vitreous, hygroscopic mass. Oxidation with 4% permanganate solution transforms it into the *sulphone*, $\text{C}_5\text{H}_{10}\text{S}\cdot\text{SO}_2$, which forms shining, prismatic crystals, m. p. 98.5—99°, belonging to the monoclinic system, and has the normal molecular weight in freezing water.

2-Methylpentamethylene sulphide, $\text{CH}_2 < \begin{array}{c} \text{CH}_2\cdot\text{CHMe} \\ \text{CH}_2\text{---CH}_2 \end{array} > \text{S}$, prepared by the action of sodium sulphide on *ae*-dibromohexane in alcoholic solution, forms a colourless liquid, b. p. 151.4—151.6° (corr.)/750 mm., D_4^{18} 0.9616, $D_4^{18.5}$ 0.9449, $n_D^{18.5}$ 1.4884, and has the normal vapour density. In chloroform solution it combines readily with bromine (2 atoms), but the product is extremely unstable. Its *methiodide*, $\text{C}_6\text{H}_{12}\text{S}\cdot\text{MeI}$, forms thin, white needles and sublimes without melting at 158—159°; the sulphide combines also with ethyl iodide, but the reaction is very slow and the product highly hygroscopic. The *compound* with mercuric chloride, $\text{C}_6\text{H}_{12}\text{S}\cdot\text{HgCl}_2$, forms slender needles, m. p. 97—98°. The corresponding *sulphoxide*, $\text{C}_6\text{H}_{12}\text{S}\cdot\text{O}$, is a pale yellow, viscous liquid, which decomposes on distillation. The *methyl hydroxide* derivative, $\text{C}_6\text{H}_{12}\text{S}\cdot\text{Me}\cdot\text{OH}$, obtained by the action of silver oxide on the methiodide in aqueous solution, is a colourless, viscous liquid; it colours litmus and rapidly absorbs carbon dioxide from the air with formation of a crystalline carbonate. The *sulphone*, $\text{C}_6\text{H}_{12}\text{S}\cdot\text{SO}_2$, forms long needles or transparent prisms, m. p. 68—68.5°, b. p. 295—296.5° (corr.)/749 mm.,

and has the normal molecular weight in boiling ether. No isomeric change occurs when the sulphide is heated in a sealed tube at 225°.

The action of hydrogen bromide on diallyl yields the crystalline *meso*- $\beta\epsilon$ -dibromohexane, m. p. 38—39°, and also a liquid dibromohexane, b. p. 108—116°/15 mm. Treatment of the latter with sodium sulphide yields a sulphide, $C_6H_{12}S$, and investigation of this and of the corresponding methiodide, mercuric chloride compound, and sulphone indicates that the liquid dibromo-derivative is a mixture composed principally of $\alpha\epsilon$ -dibromohexane. In the formation of this compound from diallyl, the additions of the two mols. of hydrogen bromide take place in different ways:

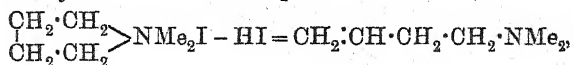


Hexamethylene Sulphide. E. GRISCHKEVITSCH-TROCHIMOVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 944—950).— $\alpha\zeta$ -Dibromohexane, $C_6H_{12}Br_2$, prepared by converting $\alpha\zeta$ -di-iodohexane, b. p. 151—155° (compare Hamonet, A., 1903, i, 306), into the corresponding diacetate and heating the latter with fuming hydrobromic acid in a sealed tube at 120°, forms a colourless liquid, b. p. 119.5—121°/18 mm.

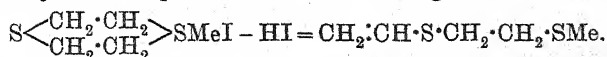
Hexamethylene sulphide, $\begin{matrix} CH_2 \cdot CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \cdot CH_2 \end{matrix} > S$, obtained in small yield by the action of sodium sulphide on $\alpha\zeta$ -dibromohexane in alcoholic solution, is a colourless, mobile liquid with the odour characteristic of cyclic sulphides, b. p. 169—171° (corr.)/747 mm., D_4^{18} 0.9743, n_D^{20} 1.5044. It forms a *methiodide*, $C_6H_{12}S, MeI$, which crystallises in long, colourless, oblique prisms, m. p. 137.5—138.5°, and a *compound* with mercuric chloride, $C_6H_{12}S, HgCl_2$, m. p. 149°. When oxidised with permanganate it gives the corresponding *sulphone*, $C_6H_{12} \cdot SO_2$, which crystallises in long, colourless needles, m. p. 70.5—71°.

When $\alpha\kappa$ -dibromodecane is heated with sodium sulphide in alcoholic solution in a sealed tube at 120—200°, very little action takes place, the formation of cyclic sulphide being detectable only by the odour of the products. T. H. P.

Rupture of the Ring of Cyclic Sulphides. E. GRISCHKEVITSCH-TROCHIMOVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 951—959).—When treated with alkali hydroxide, the methiodides of tertiary cyclic imines yield unsaturated open-chain amines,



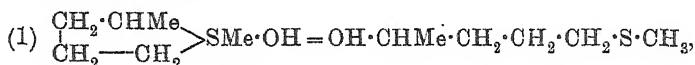
and diethylene disulphide methiodide undergoes a similar change:



The author has therefore investigated the action of alkali hydroxide on the methiodides of various cyclic sulphides which might

be expected to undergo conversion into unsaturated open-chain sulphides.

When heated with excess of 30% potassium hydroxide solution, 2-methyltetrahydrothiophen methiodide yields an unsaturated sulphide, $C_6H_{12}S$, which is a colourless, mobile liquid with a disagreeable odour, b. p. $144-146^\circ$ (corr.)/748 mm., D_4^{18} 0.8934, n_D^{18} 1.4758. It combines with four atoms of bromine, giving a highly unstable compound, and yields a methiodide, $C_6H_{12}S, MeI$, crystallising in shining prisms, m. p. $68.5-70.5^\circ$. Oxidation of the unsaturated sulphide with permanganate yields acetic acid, a trace of formic acid, and a non-volatile, viscous liquid acid, the sodium salt of which, $C_4H_7O_4SNa$, was analysed. The conclusion is drawn that the sulphide has the structure $SMe \cdot CH_2 \cdot CH_2 \cdot CH \cdot CHMe$, and that its formation is represented by the equations:



and (2) this $-H_2O = SMe \cdot CH_2 \cdot CH_2 \cdot CH \cdot CHMe$. The occurrence of a trace of formic acid among the oxidation products is probably due to the presence of a small proportion of the isomeric sulphide, $SMe \cdot CHMe \cdot CH_2 \cdot CH \cdot CH_2$.

Under similar conditions, pentamethylene sulphide methiodide is converted by the action of potassium hydroxide into the original pentamethylene sulphide, no unsaturated open-chain sulphide being obtained in this case.

The action of potassium hydroxide solution on 2-methylpentamethylene sulphide methiodide gives the unsaturated open-chain sulphide, $CHMe \cdot CH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot S \cdot CH_3$, which is a colourless liquid with an extremely disagreeable odour, b. p. $161-163^\circ$ (corr.)/748 mm., $51.5-52^\circ/15$ mm., D_4^{18} 0.8985, n_D^{18} 1.4774, and yields a methiodide, $C_7H_{14}S, MeI$, which crystallises in colourless needles volatilising without melting at $157-158^\circ$. If the unsaturated sulphide and methyl iodide are heated in acetone solution in a sealed tube at 120° , trimethylsulphonium iodide results. Oxidation of the unsaturated sulphide by means of permanganate yields acetic acid.

A mechanism similar to that given above for the conversion of 2-methyltetrahydrothiophen methiodide into unsaturated sulphide is suggested for Hofmann's transformation of the methiodides of cyclic imines into unsaturated open-chain amines. T. H. P.

Behaviour of Dihalogenated Compounds towards Alkali Sulphides. General Characteristics of the Sulphides Formed. E. GRISCHKEVITSCH-TROCHIMOVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 959-974. Compare preceding abstracts).—The properties of cyclic sulphides are compared with those of cyclic compounds containing in the ring an oxygen atom, an imino-group, oxygen and carbonyl, imino- and carbonyl groups, etc. As regards the capacity for ring-closure and for reactions in which the ring is ruptured, cyclic sulphides have much in common with the cyclic oxides and imines containing rings of the same magnitude; the

analogies advanced by von Braun (A., 1911, i, 75) do not, therefore, correspond with the experimental data.

In most cases the action of sodium sulphide on dibromo-compounds leads to the formation of three products in varying relative proportions: the unimolecular sulphide, a product which contains sulphur and halogen and is probably a dihalogenated thio-ether, and a polymerised sulphide.

The cyclic sulphides obtained by the author by the action of sodium sulphide on dibromo-compounds contain from three to ten carbon atoms and rings with four to seven members. They are colourless, mobile liquids with unpleasant, characteristic odours, and they distil undecomposed and are readily volatile in a current of water-, alcohol-, or ether-vapour. They are insoluble in water, but mix in all proportions with ordinary organic solvents. Chemically, they are analogous to the aliphatic thio-ethers, and they are readily oxidised by permanganate to the corresponding sulphones and by dilute nitric acid to sulphoxides. With methyl iodide they form crystalline methiodides, and they combine readily with mercuric chloride and with bromine, the products in the latter case being very unstable; they do not react with benzoyl chloride, alkalis, or sodium.

With homologues derived from trimethylene, tetramethylene, and pentamethylene sulphides by replacement of one or two hydrogen atoms by methyl groups, each of the latter raises the boiling point by about 10° . The introduction of an extra methylene group into the ring raises the boiling point by about 26° . The boiling points of isomeric sulphides containing rings of different magnitudes vary very considerably. The specific gravities of homologues derived from cyclic sulphides by replacement of hydrogen atoms by methyl groups form a gradually diminishing series, whilst those of isomeric sulphides increase regularly as the magnitude of the ring increases.

Calculation of the atomic refraction of sulphur by subtraction of the sum of the atomic refractions of the carbon and hydrogen atoms from the molecular refractions of the cyclic sulphides leads to values lying between 7.40 and 8.41, the mean being 7.84, which is very near to the value, namely, 7.65, of the atomic refraction of sulphur in compounds of the thiophen series. This result was scarcely to be expected in view of the fact that, with oxygen, nitrogen, etc., the magnitude of the atomic refraction varies within comparatively wide limits as the chemical function of the atom and the character of the compound change, and that whereas the sulphur atom is incapable of changing its valency in thiophen, in the cyclic sulphides it readily assumes quadri- or sexa-valency.

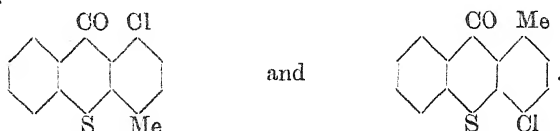
In cyclic sulphones, the atomic refraction of oxygen is calculated to have the mean value 0.45.

T. H. P.

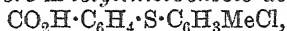
The Thioxanthone- and Benzophenone-sulphone Series. F. ULLMANN and OTTO VON GLENCK (*Ber.*, 1916, 49, 2487—2514).—The authors deemed it to be of interest to prepare thioxanthone derivatives with auxochromic groups adjacent

to the chromophoric carbonyl group, and have chosen as a convenient source of such compounds 1-chlorothioxanthenes. These can be prepared readily by the condensation of chlorobenzenes with *o*-thiolbenzoic acid (Davis and Smiles, T., 1910, **97**, 1290).

When *o*-thiolbenzoic acid is condensed with *p*-chlorotoluene, it is possible that both 1-chloro-4-methyl- and 4-chloro-1-methylthioxanthenes might be formed, only the former being of interest in this research:

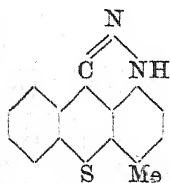


Both are formed, to the extent of 60% of the desired one and 40% of the other, as subsequent condensations show, but the mixture appears at first sight to be a perfectly homogeneous substance having a constant m. p., 148—148·5°. It is extremely difficult to separate these, but by taking advantage of the fact that the 1-chloro-compound is comparatively non-volatile at above 200° in a vacuum, whilst the 4-chloro-compound does not react any further with thiolbenzoic acid, the two individuals have been isolated. 1-Chloro-4-methylthioxanthene forms doubly refractive, colourless needles, m. p. 150—150·5°, and 4-chloro-1-methylthioxanthene has m. p. 142·5—143°. The latter has been synthesised as follows: 4-chloro-3-nitrotoluene is reduced to 4-chloro-*m*-toluidine by means of iron turnings and acetic acid; this is converted into 4-chloro-3-iodotoluene, b. p. 249°, which is then boiled with *o*-thiolbenzoic acid, potassium carbonate, and a trace of copper acetate in amyl alcohol. The 2-*p*-chloro-*m*-tolylthiolbenzoic acid,



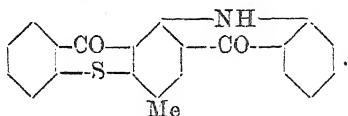
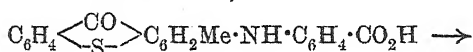
which is thus formed, in pearly needles, m. p. 193°, yields the desired 4-chloro-1-methylthioxanthene when dissolved in sulphuric acid monohydrate.

For the purpose of further condensations, the mixture of the isomerides is suitable, as the 4-chloro-compound is inactive. Thus, with hydrazine hydrate in alcohol, in the presence of a trace of cuprous chloride, at 180°, the anhydride of 4-methylthioxanthonyl-1-hydrazine (annexed formula) is produced in colourless spikes, m. p. 251°. With boiling aniline and potassium

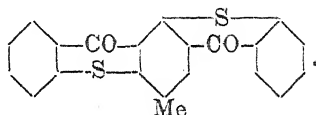
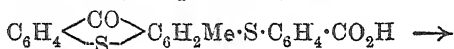


acetate and a trace of copper, 1-anilino-4-methylthioxanthene is formed in pale orange needles, m. p. 127°. Similarly, *p*-toluidine gives 1-*p*-toluidino-4-methylthioxanthene, reddish-orange needles, m. p. 132°, and *p*-toluenesulphonamide forms 1-*p*-toluenesulphonylamino-4-methylthioxanthene, in pale yellow, flat prisms, m. p. 191·5°. The last-named yields 1-amino-4-methylthioxanthene on hydrolysis with warm, concentrated sulphuric acid, in orange-yellow needles and prisms, m. p. 134°. The isomeric 4-amino-1-methylthioxanthene is obtained in canary-yellow prisms, m. p. 184°, by condensing *o*-thiolbenzoic acid with *p*-toluenesulpho-*p*-toluidide in

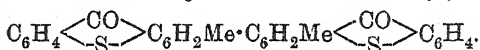
fuming sulphuric acid. Anthranilic acid condenses in boiling amyl alcohol to form 4-methylthioxanthonyl-1-anthranilic acid, orange-coloured, rhombic leaflets, m. p. 274°, which condenses still further in concentrated sulphuric acid to form 4-methylthioxanthone-2:1-acridone, thus:



The latter crystallises in pale yellow clusters of very slender needles, m. p. 297·5°. *o*-Thiolbenzoic acid yields *o*-4-methylthioxanthonylthiolbenzoic acid in yellow prisms, m. p. 248°, and this also condenses in sulphuric acid to give 4-methyldithioxanthone, in golden-yellow scales, m. p. 272·5°, thus:

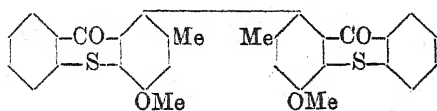


Finally, condensation between two molecules of 1-chloro-4-methylthioxanthone to 4:4'-dimethyl-1:1'-dithioxanthonyl,



takes place when the substance is boiled with naphthalene and copper powder. This crystallises in pale yellow, flat prisms, m. p. 332°.

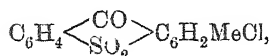
6-Chloro-*m*-methoxytoluene condenses more readily with *o*-thiolbenzoic acid than *p*-chlorotoluene does, and yields exclusively 1-chloro-4-methoxy-2-methylthioxanthone, in pale yellow prisms or slender needles, m. p. 185°. Further condensations were effected with this compound in order to determine the influence of the methoxy-group on the colour. 4-Methoxy-2-methylthioxanthonyl-1-anthranilic acid crystallises in slender, orange needles, m. p. 285°. 1-Anilino-4-methoxy-2-methylthioxanthone forms long, yellow needles from acetic acid, or rhombic leaflets from alcohol, m. p. 183°. 1-*p*-Toluenesulphonylamino-4-methoxy-2-methylthioxanthone, yellow prisms, m. p. 188°, yields 1-amino-4-methoxy-2-methylthioxanthone, brick-red needles, m. p. 144°, on hydrolysis. 4:4'-Dimethoxy-2:2'-dimethyl-1:1'-dithioxanthonyl (annexed formula)



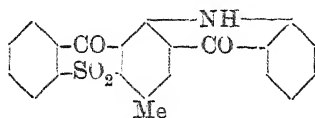
is obtained by boiling the chloro-compound with naphthalene and copper powder, in pale yellow, slender needles, m. p. 372°, a small amount of

4-methoxy-2-methylthioxanthone, m. p. 167—168°, being formed at the same time.

Several of these thioxanthenes have been oxidised to benzophenonesulphones by means of 30% hydrogen peroxide in glacial acetic acid or potassium persulphate in concentrated sulphuric acid. 1-Chloro-4-methylbenzophenonesulphone,

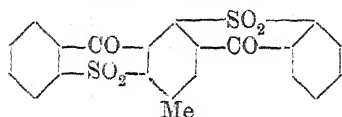


crystallises in colourless prisms or tablets, m. p. 184—185° (the 4-chloro-1-methyl isomeride must also be contained in this), and condenses with anthranilic acid to form 1-anthranilo-4-methylbenzophenonesulphone, in orange-red needles or prisms, m. p. 317°. This condenses further in concentrated sulphuric acid to 4-methylbenzophenonesulphone-2:1-acridone (annexed formula), which



crystallises in pale ruby-red, glistening needles, m. p. 303°. 1-Chloro-4-methoxy-2-methylbenzophenonesulphone forms pale yellow needles, m. p. 183°. 1-Anilino-4-methoxy-2-methylbenzophenonesulphone crystal-

lises in garnet-red prisms, m. p. 192—193°, and the corresponding 1-p-toluidino-compound in ruby-red cubes, m. p. 184°. 4-Methyl-



dibenzophenonedisulphone (annexed formula), the product of the oxidation of 4-methyldithioxanthone, forms almost colourless needles, m. p. 328°.

All the melting points are J. C. W.

“corrected.”

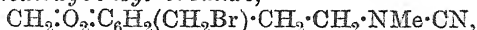
[iso-Nortropinone]. J. HOUBEN and ALEXANDER PFAU (*Ber.*, 1916, 49, 2745. Compare this vol., i, 25).—A compound referred to in the discussion was designated “nortropinone.” It should have been *isonortropinone*. J. C. W.

Degradation of Scopoline. K. HESS (*Ber.*, 1916, 49, 2745. Compare this vol., i, 52).—A question of priority. J. C. W.

Rupture of the Ring [Nitrogen] in Hydrohydrastinine and Hydrocotarnine by means of Cyanogen Bromide. J. VON BRAUN (*Ber.*, 1916, 49, 2624—2629).—When 2-methyl-1:2:3:4-tetrahydroisoquinoline is treated with cyanogen bromide, the elements of this agent are attached at the 1 and 2 positions, and the ring is ruptured. Although the *o*-β-cyanomethylaminoethylbenzyl bromide which is thus formed has not been purified, it seemed worth while to apply the same reaction to alkaloids of the same type, particularly as the nitrogen ring is thereby opened at a point other than that affected in the Hofmann degradation.

Hydrohydrastinine, when treated with cyanogen bromide in

ether, yields the expected product, 2- β -cyanomethylaminoethyl-4:5-methylenedioxybenzyl bromide,



as a snow-white mass, m. p. 109° , which is not very stable, especially in the light and in contact with hydroxylic solvents. As an active bromide, it readily reacts with piperidine to form the compound, $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2\cdot\text{CH}_2\cdot\text{C}_5\text{H}_{10}\text{N}$, m. p. 155° , and with pyridine to form the quaternary bromide, $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2\cdot\text{CH}_2\cdot\text{C}_5\text{H}_5\text{NBr}$, m. p. 209° . A similar quaternary bromide of hydrohydrastinine, m. p. 165° , accompanies the bromide in the introductory reaction.

Hydrocotarnine gives an even more reactive product, 2- β -cyanomethylaminoethyl-6-methoxy-4:5-methylenedioxybenzyl bromide, m. p. 74° , which readily polymerises to a glassy mass when warmed on the water-bath.

J. C. W.

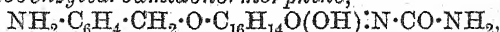
Insoluble Morphine in Crude Opium. P. CARLES (*J. Pharm. Chim.*, 1917, [vii], 15, 44—47).—The author has not been able to obtain any evidence of the presence of an insoluble modification of morphine in crude opium. Statements by various observers that such a modification exists are possibly due to the fact that large masses of opium are not readily penetrated by water or dilute alcohol, and that small quantities of solvent fail to extract the whole of the morphine.

W. P. S.

The Morphine Alkaloids. IV. J. VON BRAUN and K. KINDLER (*Ber.*, 1916, 49, 2655—2663. Compare A., 1914, i, 1138; 1916, i, 500, 665).—It was shown in the case of aminocyanonorcodeine that the physiological activity of codeine, which is lost by removing the basic properties of the ring-nitrogen, is not restored by the introduction of an amino-group in the aromatic nucleus. The effect of the transposition of a hydroxyl group is found to be practically the same; although the group is still present in another part of the molecule, the physiological activity is greatly lessened. Furthermore, the properties of codeine cannot be reproduced by building up a simpler molecule containing the various "groups" of codeine, that is, a methoxylated benzene ring, a nitrogen ring with methylated nitrogen, and an alcohol group. It appears that the deciding factor in the case of codeine and morphine is the position of the nitrogen with regard to the bridged hexamethylene ring (A., 1914, i, 1138).

Although the $>\text{N}[\text{CH}_2]_3\cdot\text{OBz}$ grouping is associated with many anaesthetics, it is found that in norcodeine it has no such influence.

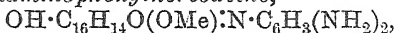
Cyanonormorphine reacts with *p*-nitrobenzyl chloride in the presence of sodium ethoxide to form *p*-nitrobenzylcyanonormorphine, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_{16}\text{H}_{14}\text{O}(\text{OH})\cdot\text{N}\cdot\text{CN}$, m. p. 229° , which may be hydrolysed to *p*-nitrobenzylnormorphine, pale yellow crystals, m. p. 180° (hydrochloride, decomp. 297°), or converted into *p*-aminobenzylcarbamidonormorphine,



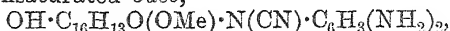
colourless leaflets, m. p. 297° , by warming with stannous chloride and hydrochloric acid.

Norcodeine reacts readily with *op*-dinitrobenzobenzene to form

op-dinitrophenylnorcodeine, deep yellow, m. p. 265°, which is easily reduced to op-diaminophenylnorcodeine,



m. p. 233°. This forms an *acetyl* compound, m. p. 144—146°, which reacts readily with cyanogen bromide, suffering rupture of the nitrogen ring, and giving an unsaturated *cyanamide*, $\text{C}_{30}\text{H}_{30}\text{O}_6\text{N}_4$, m. p. 148—149°, and this compound may be hydrolysed to an unsaturated *base*,



m. p. 168—169°. *p*-Bromonitrobenzene reacts with norcodeine very sluggishly, giving *p*-nitrophenylnorcodeine, m. p. 212°.

α -Chlorocyanonorcodide reacts with dimethylamine to form dimethylaminocyanonorcodide, $\text{NMe}_2\cdot\text{C}_{16}\text{H}_{14}\text{O}(\text{OMe})\cdot\text{N}\cdot\text{CN}$, m. p. 192° (*hydrochloride*, m. p. 266°; *picrate*, m. p. 190°; *methiodide*, m. p. 203°), and this may be hydrolysed to dimethylaminonorcodide, m. p. 128° (*picrate*, m. p. 218°; *platinichloride*, m. p. 275—276°). For comparison with this, α -chlorocodide was converted into dimethylaminocodide, $\text{NMe}_2\cdot\text{C}_{16}\text{H}_{14}\text{O}(\text{OMe})\cdot\text{NMe}$, m. p. 118° (*platinichloride*, m. p. 250°), and diethylaminocodide, m. p. 102° (*platinichloride*, decomp. 240°). Dimethylaminonorcodide unites with ethylene oxide to form dimethylamino-N- β -hydroxyethylnorcodide, $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{N}\cdot\text{C}_{16}\text{H}_{14}\text{O}(\text{OMe})\cdot\text{NMe}_2$, as a very hygroscopic substance, m. p. 85°, which yields a yellow *platinichloride*, m. p. 255°.

Methylthalline (6-methoxy-1-methyl-1:2:3:4-tetrahydroquinoline) is best separated from the product of the action of methyl iodide on thalline by benzoylating, and extracting the unaffected tertiary base by sulphuric acid. It has b. p. 150—151°/10 mm., forms a *picrate*, leaflets, m. p. 164°, and combines with formaldehyde to give 6-methoxy-8-hydroxymethyl-1-methyl-1:2:3:4-tetrahydroquinoline, $\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_2(\text{OMe})\cdot\begin{matrix} \text{CH}_2-\text{CH}_2 \\ \text{NMe} \text{ } \text{CH}_2 \end{matrix}$, as a yellow, viscous oil, b. p. 203—207°/10 mm.

Norcodeine reacts with γ -bromopropyl benzoate (A., 1913, i, 720) under the conditions for the alkylation of norcodeine recently devised (A., 1916, i, 665) to form γ -benzoyloxypropylnorcodeine, $\text{OH}\cdot\text{C}_{16}\text{H}_{14}\text{O}(\text{OMe})\cdot\text{N}\cdot\text{C}_3\text{H}_6\cdot\text{OBz}$, m. p. 47°. This yields a *hydrochloride*, a *picrate*, m. p. 118—119°, and a *methiodide*, m. p. 169—170°, and may be hydrolysed easily to γ -hydroxypropylnorcodeine, m. p. 133° (*picrate*, yellow leaflets, m. p. 120—121°).

J. C. W.

Condensation of Pyrrole and 1-Methylpyrrole with Formaldehyde: Preparation of Glycols of the Pyrrole Series.

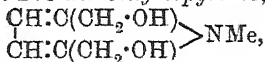
V. V. TSHELINCEV and B. V. MAKOROV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 748—779).—The condensation of pyrrole with formaldehyde in presence of an acid (compare Pictet and Rilliet, A., 1907, i, 445) yields a non-oxygenated product containing one formaldehyde residue to one pyrrole residue. The results of experiments on the condensation of pyrrole with acetone (Tschelincev and Tronov, this vol., i, 91, 93) and of those described below indicate

that the structure of the above compound is represented by the annexed formula. Treatment of this compound with hydrochloric acid in acetone yields a cinnabar-coloured, amorphous substance, which is turned yellow by potassium hydroxide, and gives analytical results corresponding approximately with the formula $C_{30}H_{36}O_3N_4$. By hydrochloric acid in ethyl-alcoholic solution, the same product is converted into an orange-yellow, gelatinous substance of the composition $C_{23}H_{34}O_6N_4$. Owing to their slight solubility and ready alteration, these products were not further investigated.

The above product, $(C_5H_5N)_n$, is also obtained by the condensation of pyrrole (1 mol.) and 4% formaldehyde solution (1 mol.) in absence of acid at the ordinary temperature. When, however, under these conditions 20% formaldehyde solution is employed, the result of the condensation is an almost colourless substance which has the composition $C_{27}H_{30}O_3N_4$ and the molecular weight 505 in freezing bromoform, the calculated value being 458. This substance differs from those obtained in presence of an acid by its ready solubility in most solvents; when treated with hydrochloric or sulphuric acid, it is converted into a bright yellow, amorphous, flocculent substance similar to those described above.

More definite results are obtained when the condensation is carried out in presence of potassium carbonate at 80–90°. Under these conditions, pyrrole and formaldehyde yield the glycol, 2:5-dimethylolpyrrole, $\begin{matrix} \text{CH:C(CH}_2\cdot\text{OH)} \\ \text{CH:C(CH}_2\cdot\text{OH)} \end{matrix} > \text{NH}$, which forms long, colourless needles, m. p. 117–118°, exhibits normal cryoscopic behaviour in water, and by inorganic or organic acids is converted into an orange-yellow, voluminous, flocculent substance, $C_{18}H_{22}O_5N_2$. When oxidised with silver oxide, this glycol gives pyrrole-2:5-dicarboxylic acid, which was identified by means of its methyl ester and by the methyl ester of its 3:4-dibromo-derivative (compare Ciamician and Silber, A., 1886, 938).

The glycol, 1-methyl-2:5-dimethylolpyrrole,



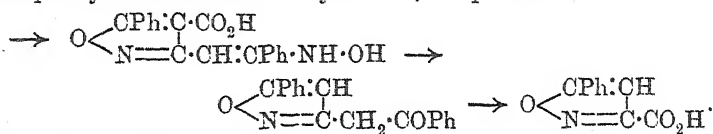
obtained by condensation of 1-methylpyrrole and formaldehyde in presence of potassium carbonate, forms spherical, drusy masses of white needles, m. p. 113–114°, exhibits normal cryoscopic behaviour in water, and is converted into an insoluble, orange, gelatinous, flocculent substance, $C_{19}H_{16}O_3N$, by the action of acids. On oxidation with sodium peroxide and permanganate, the glycol yields 1-methylpyrrole-2:5-dicarboxylic acid (compare Fischer, A., 1913, i. 1225); the methyl ester of this acid, $C_9H_{11}O_4N$, m. p. 80–81°, and methyl 3:4-dibromo-1-methylpyrrole-2:5-dicarboxylate, $C_9H_9O_4NBr_2$, m. p. 159°, were prepared. T. H. P.

New Method of Preparing Pyrrole-2:5-dicarboxylic Acids.
V. V. TSHELINCEV and B. V. MAKOROV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 779–790).—These acids may be obtained in good

yields by oxidation of the corresponding glycols, which are themselves readily obtainable by the condensation of pyrroles with formaldehyde in presence of potassium carbonate (compare preceding abstract).
T. H. P.

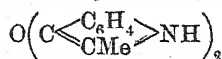
Inactivity of the γ -Carbonyl of certain Pyrone and Pyridone Derivatives. IV. SCHÖTTLE (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 530—532).—The inactivity of the γ -carbonyl of pyrones towards hydroxylamine and phenylhydrazine has been established by a number of investigations. In most cases, these reagents either do not react or else replace the oxygen of the nucleus. The author now finds that similar inactivity towards these two reagents is exhibited by the γ -carbonyl group in 2:6-diphenylpyridone, 4-hydroxypyridine-2:6-dicarboxylic acid, 4-hydroxy-1-methylpyridine-2:6-dicarboxylic acid, 1-phenoxy-pyridone, and 1-phenylpyridone, the unaltered compound being recoverable in all cases.

According to these results, in the reaction between hydroxylamine or phenylhydrazine with lactamic derivatives of benzoyl-dehydracetic acid (A., 1915, i, 695), there is no possibility of the formation of oxime or phenylhydrazone at the γ -carbonyl group. If such reaction were to take place, the formation of a compound of the type $O \begin{smallmatrix} \text{CPh} \cdot \text{C} \cdot \text{CO} \cdot \text{N} \cdot \text{OH} \\ \text{N} = \text{C} \cdot \text{CH} \cdot \text{CPh} \end{smallmatrix}$ would be expected, and this, when heated with concentrated hydrochloric acid and subsequently oxidised, should undergo decompositions, resulting in the formation of 5-phenylisooxazole-3-carboxylic acid, m. p. 162°:



The acid actually obtained by the author under these conditions has, however, m. p. 177—178°, and, when distilled, does not yield 5-phenylisooxazole or cyanoacetophenone. Support is thus afforded to the formulation of the reaction previously given by the author (*loc. cit.*).
T. H. P.

Auto-oxidation of Indoles in Daylight. OSKAR BAUDISCH and ARTHUR BARON HOSCHEK (*Ber.*, 1916, **49**, 2579—2583).—When suspensions of 2-methylindole in water are exposed to the light in the presence of oxygen, the solid and liquid become very dark brown in time, and the gas is absorbed. Some details of the examination of products obtained in this way in the bright sunlight of the Alps are given. It appears that the first product is a red, amorphous polymeride, which then suffers partial photolysis and oxidation to *di*-2-methyl-3-indolyl ether,



which forms long, sulphur-yellow, rhombic crystals, m. p. 210°. This ether then undergoes further hydrolysis and oxidation to

N-acetyl-anthranilic acid and anthranilic acid itself. The two stages in the oxidation can be realised also by boiling the red powder with alkaline permanganate.

Indole seems to behave in a similar manner, which is significant in view of the fact that methyl anthranilate and indole are known to occur together in some plants, for example, in *Robinia pseudo-acacia*, L. J. C. W.

Condensation of Indoles with Aromatic Aldehydes. ARTHUR BARON HOSCHEK (*Ber.*, 1916, 49, 2584—2588).—In the course of some experiments on the auto-oxidation of 2-methylindole (preceding abstract), it seemed possible at first that *o*-acetylaminobenzaldehyde might be formed and then condense with the unchanged base. Condensations of *o*-aminobenzaldehyde with indole and 2-methylindole, and of *o*-acetylaminobenzaldehyde with the latter base, have therefore been effected by heating the substances together in sealed tubes. No reaction seems to take place at lower temperatures, but normal benzylidene compounds are formed at about 140—160°.

3 : 3'-*o*-Aminobenzylidenedi-indole (*di*-3-indolyl-*o*-aminophenylmethane), $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \left(\text{C} \begin{array}{c} \swarrow \searrow \\ \text{CH} \cdot \text{NH} \end{array} \text{C}_6\text{H}_4 \right)_2$, forms pale yellow leaflets, m. p. 97°, and yields a brick-red *hydrochloride*, m. p. 244°. 3 : 3'-*o*-Aminobenzylidenedi-2-methylindole is a snow-white powder, m. p. 250°, and its *hydrochloride*, 3HCl, forms pearly needles and leaflets. 3 : 3'-*o*-Acetylaminobenzylidenedi-2-methylindole is a white substance, m. p. 210°, which becomes red in contact with traces of acids. J. C. W.

Scission of the Hydrogenated Indole and Quinoline Rings by Reduction. III. **Substituted Hydroindole Bases.** J. VON BRAUN, K. HEIDER, and L. NEUMANN. (*Ber.*, 1916, 49, 2613—2624. Compare A., 1916, i, 421, 742).—It was recently shown that when the quaternary methochloride of dihydroindole is treated with sodium amalgam, it is reduced to 1-methyldihydroindole, β -dimethylaminoethylbenzene, and *o*-dimethylaminoethylbenzene concurrently. Some dihydroindoles, loaded with side-chains in the pyrrole ring, have now been examined under the same conditions in order to test the influence of substituents on the reduction. The results tabulated below show how great the influence is, especially on the yield of the ortho-substituted dimethylaniline. Such a difference in the stability of the indole ring is not apparent in the case of the Hofmann reaction.

	Tertiary cyclic base.	Substituted dimethyl- aniline.	Aryl- aliphatic amine.
2 : 3-Dihydroindole	75%	8%	17%
2-Methyl-2 : 3-dihydroindole	40	40	20
3-Methyl-2 : 3-dihydroindole	76	trace	24
2 : 3 : 3'-Trimethyl-2 : 3-dihydroindole...	90	10	trace
Hexahydrocarbazole	88	3.6	8.4

The methochloride of dihydromethylketole (1:1:2-trimethyl-2:3-dihydroindolium chloride) yields: (1) 1:2-dimethyl-2:3-dihydroindole, which is isolated as the di-indylmethane compound,

$\text{CH}_2(\text{C}_6\text{H}_3\langle\text{CH}_2\text{NMe}_3\rangle\text{CHMe})_2$, m. p. 120°; (2) *o*-dimethylaminopropylbenzene, b. p. 104—105°/17 mm., which forms a *picrate*, m. p. 150°, a *platinichloride*, m. p. 146°, and a *methiodide*, m. p. 148°; (3) β -dimethylaminopropylbenzene, which is obtained in the form of the *methiodide*, $\text{CH}_3\text{Ph}\cdot\text{CHMe}\cdot\text{NMe}_3\text{I}$, m. p. 228°, and identified by conversion into trimethylamine and the known *isoallylbenzene*, $\text{CHPh}\cdot\text{CHMe}$, in the usual way.

Dihydroscatole is converted into the methiodide, 1:1:3-trimethyl-2:3-dihydroindolium iodide, m. p. 203—204°, and, after treating this with silver chloride, sodium amalgam, and formaldehyde, and separating the solid methylene compound, a trace of *o*-dimethylaminoisopropylbenzene (*picrate*, m. p. 139°) and also β -dimethylaminoisopropylbenzene, $\text{CHPhMe}\cdot\text{CH}_2\cdot\text{NMe}_3$, b. p. 97—98°/18 mm., are found in the volatile products. The latter forms a *methiodide*, m. p. 158°, which yields trimethylamine and α -methylstyrene, $\text{CPhMe}\cdot\text{CH}_2$, b. p. 163—164°/752 mm., when the corresponding hydroxide is distilled.

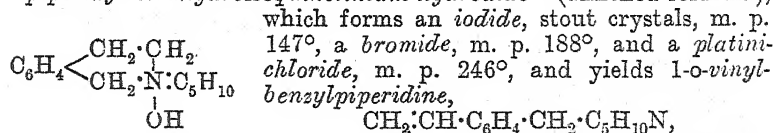
2:3:3-Trimethyl-2:3-dihydroindole has furnished the following new compounds: the methylene compound of the methiodide of the *tert.*-base, $\text{CH}_2(\text{C}_6\text{H}_3\langle\text{CMe}_2\text{NMe}_2\text{I}\rangle\text{CHMe})_2$, m. p. above 300° (decomp.), and almost pure *o*-dimethylaminoisooamylbenzene, b. p. 122—123°/23 mm., which forms a *hydrochloride*, m. p. 164°, and a *picrate*, yellow needles, m. p. 182°.

Hexahydrocarbazole (Borsche, A., 1908, i, 365) forms a quaternary *methiodide*, $\text{C}_{14}\text{H}_{20}\text{NI}$, m. p. 187°, which may be converted into 1-methylhexahydrocarbazole, b. p. 162°/24 mm., in the usual way, but it is believed that during the distillation a small portion of the substance suffers rupture of the *N*-ring, giving an impurity which makes the constants for the expected base and its salts indefinite. The base condenses with formaldehyde to yield the compound, $\text{CH}_2(\text{C}_6\text{H}_3\langle\text{C}_6\text{H}_{10}\text{NMe}\rangle_2)$, m. p. 116—117°, which forms a *hydrochloride*, m. p. 110°, and a *methiodide*, m. p. 180°. When the methiodide is treated with silver chloride, sodium amalgam, and formaldehyde, the same methylene compound is obtained in a high yield, and from the volatile bases can be separated *o*-dimethylaminophenylcyclohexane, which is characterised by a *platinichloride*, m. p. 169—170°, a *picrate*, m. p. 160°, and also the *methiodide*, $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_{10}\cdot\text{NMe}_3\text{I}$, m. p. 119°. When the ammonium hydroxide corresponding with this is distilled, the main product is 2:3:4:5-tetrahydrodiphenyl (1-phenyl- Δ^1 -cyclohexene), b. p. 132°/26 mm., D_4^{20} 0.9931, n_D^{20} 1.57179 (compare Auwers and Treppmann, A., 1915, i, 789), mixed with some *o*-dimethylaminophenylcyclohexane (*o*-phenylcyclohexyldimethylamine), $\text{C}_6\text{H}_{10}\text{Ph}\cdot\text{NMe}_3$, which is characterised by a *picrate*, m. p. 164—165°. J. C. W.

The Relative Stability of the Rings in Cyclic Bases under the Conditions of the Hofmann Reaction. J. VON BRAUN (*Ber.*, 1916, **49**, 2629—2642).—Researches during recent years on the action of cyanogen bromide on cyclic compounds containing nitrogen have shown that the resistance offered to the disruption of the ring increases in the order: dihydroisoindole and tetrahydroisoquinoline, pyrrolidine, piperidine, and tetrahydroquinoline. It seemed to be of interest, therefore, to devise a scheme by which the stability of these ring systems during the Hofmann reaction could be tested, and salts like the "pyrrolidylpiperidinium" bromide recently described (A., 1916, i, 632) offer the way. The hydroxides of four such compounds have been heated, and the weaker of the two rings determined by an examination of the products. It is found, again, that the stability of the ring increases in the order: tetrahydroisoquinoline, dihydroisoindole, pyrrolidine, piperidine, and dihydroindole and tetrahydroquinoline. This is remarkable, as the two reactions are so different, and it suggests that the stability of the ring is in some way intimately connected with the exercise of all the forces in the molecule as a whole.

The Hofmann reaction is usually defined as the production of an unsaturated, tertiary, open-chain base from a cyclic, quaternary ammonium hydroxide by the elimination of water, but the present experiments show that the loss of water is a secondary consideration. Hydroxy-amines are frequently formed.

Tetrahydroisoquinoline is warmed with *ae*-dibromo(or di-iodo)-pentane and aqueous sodium hydroxide, and so converted into "*piperidyltetrahydroisoquinolinium hydroxide*" (annexed formula),



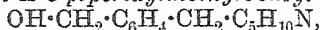
on distillation under reduced pressure. This base has b. p. 151—152°/16 mm., and forms a *hydrochloride*, m. p. 205°, a *platinichloride*, an *aurichloride*, yellow leaflets, m. p. 108°, a *picrate*, m. p. 150°, and a *methiodide*, m. p. 161°. The constitution of the base is determined by its reaction with cyanogen bromide. This gives an oil with an odour like benzyl bromide, consisting of equivalent quantities of 1-cyanopiperidine, b. p. 105°/10 mm., and *o*-vinylbenzyl bromide, which are separated by the addition of trimethylamine, whereby the *methobromide* of *o*-vinylbenzyltrimethylamine, m. p. 215°, is precipitated (compare Emde, A., 1912, i, 801), thus: $\text{CH}_2 \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_5\text{H}_{10}\text{N}^+ + \text{BrCN} = \text{CH}_2 \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{Br} + \text{CN} \cdot \text{C}_5\text{H}_{10}\text{N}$.

From *ad*-dibromobutane, "*pyrrolidyltetrahydroisoquinolinium*" *bromide*, m. p. 168°, can be prepared, and the corresponding hydroxide converted into 1-*o*-vinylbenzylpyrrolidine by distillation. This base has b. p. 147—148°/21 mm., and forms a *picrate*, m. p. 110—111°, a *platinichloride*, leaflets, m. p. 155°, and a *methiodide*, m. p. 129°. Its constitution is again determined by the action of cyanogen bromide, which produces 1-cyanopyrrolidine, *o*-vinyl-

benzyl bromide, and a *quaternary bromide*, $C_{22}H_{26}NBr$, m. p. 100° , compounded of the latter and undecomposed *o*-vinylbenzylpyrrolidine.

o-Xylylene dibromide gives rise to "*dihydroisoindolyltetrahydroisoquinolinium*" bromide, $C_6H_4 \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot NBr \end{smallmatrix} \begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix} C_6H_4$, m. p. 210° , and the corresponding hydroxide mainly yields *N*-*o*-vinylbenzyl*dihydroisoindole* on heating, as an oil which suffers partial decomposition on redistillation; b. p. $217-218^\circ/18$ mm., m. p. 41° ; *hydrochloride*, m. p. 177° ; *picrate*, m. p. 121° ; *methiodide*, m. p. 175° .

The action of heat on *o*-xylenepiperidinium hydroxide ["*dihydroisoindolylpiperidinium*" hydroxide] was investigated by Scholtz and Wolfrum (A., 1910, i, 773). It is now suggested that the primary product is *o*-piperidylmethylbenzyl alcohol,



which has m. p. 71° , b. p. $181-182^\circ/17$ mm. The crude distillate, b. p. $190-210^\circ$ (chiefly), $210-300^\circ$, deposits this solid, and the remaining oil possibly contains Scholtz's amylenyldihydroisoindole, $C_6H_4 \begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix} N \cdot C_5H_6 \cdot CH : CH_2$, in the more volatile portions, but the less volatile oils are certainly decomposition products of the amino-alcohol. The latter forms a *hydrochloride*, m. p. $169-170^\circ$, a *platinichloride*, m. p. 197° , an *aurichloride*, m. p. 103° , a *picrate*, m. p. 140° , a *methiodide*, m. p. 135° , an *acetate*, m. p. 242° , the *picrate* of a *benzoate*, m. p. 120° , and the *platinichloride* of an *anisate*, m. p. 188° . The amino-alcohol also changes into the hydrochloride of the corresponding derivative of benzyl chloride when heated with hydrochloric acid, and the free chloro-base changes quickly into *o*-xylenepiperidinium chloride on warming.

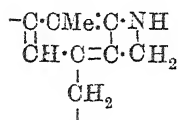
"*Dihydroisoindolylpyrrolidinium*" bromide, m. p. $165-166^\circ$, is prepared in the same way. The hydroxide did not yield a solid product on heating, but it was obvious that the pyrrolidine ring had not suffered much disruption.

"Piperidylpyrrolidinium" hydroxide (*loc. cit.*), when distilled, yields 1- δ -hydroxybutylpiperidine, b. p. $133-134^\circ/20$ mm. (*ibid.*), and a somewhat larger quantity of a fraction, b. p. $176-180^\circ$ /atmos., which consists of a mixture of 1- Δ^7 -butenylpiperidine and 1- Δ^8 -pentenylpyrrolidine. This mixture was hydrogenated, and then, by careful fractionation, 1-amylpyrrolidine, b. p. 179° , was isolated. This base was also synthesised by the action of $\alpha\delta$ -dibromobutane on *n*-amylamine. It forms a *picrate*, reddish-yellow needles, m. p. $118-119^\circ$, and a hygroscopic *methiodide*, m. p. $169-170^\circ$.

J. C. W.

Condensation of Amines with Formaldehyde. P. M. KRONEBERG (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 305-309).—Investigation of the condensation of *o*-toluidine with formaldehyde in presence of dilute (1:6) sulphuric acid (compare Nastukov and Malkin, A., 1912, i, 962; Nastukov and Kroneberg, *ibid.*) shows

that the melting point of the product varies with the temperature at which the reaction takes place. The base obtained in the cold has m. p. 183—185°, gives the molecular weight 1043 in freezing nitrobenzene, and on dry distillation yields *o*-toluidine, *m*-xylylidine, and diaminoditolylmethane. The base is formed according to the equation $(C_7H_9N + 2CH_2O)_8 = (2H_2O + C_6H_5N)_8$, and may be regarded as a polymeric form of the residue



(annexed formula). When the condensation takes place at 65—70°, the product melts at 115—116° (112—113°), and when the reacting mixture is boiled, the resultant melting point is 110—111°. Further, all these products undergo a gradual fall in melting point on keeping, the melting point 183—183.5° changing to 103—104°. The melting points of the products given by formaldehyde and other bases in presence of dilute sulphuric acid in a boiling solution are: *m*-toluidine, 169—170°; xylidine, 58.5—59.5°; and *o*-anisidine, 133—134°.

It is evident that the molecular weight of the product given by such a condensation is a function of the temperature of the reaction, and that, at temperatures below the boiling point of the solution, the base obtained is unstable and undergoes molecular change in the air. The instability of the base obtained at the ordinary temperature is shown by the fact that its molecular weight is 129 in boiling pyridine (*loc. cit.*) and 1043 in freezing nitrobenzene. The products of the condensation of formaldehyde with other bases are being investigated.

T. H. P.

Rhodanines, Parabanic Acids, and Related Substances.

KARL H. STIEGER (*Monatsh.*, 1916, **37**, 635—658).—An extension of the earlier investigations (Andreasch, A., 1910, i, 694; 1908, i, 683; 1907, i, 233, etc.).

3-isoAmylrhodanine, $\begin{array}{c} S-CH_2 \cdot CO \\ | \\ N \cdot CH_2 \cdot CH_2 \cdot CHMe_2 \end{array} > N \cdot CH_2 \cdot CH_2 \cdot CHMe_2$, obtained by

mixing isoamylamine, potassium hydroxide solution, and carbon disulphide, and treating the resulting solution of potassium isoamylidithiocarbamate with ethyl chloroacetate, is a viscous, yellow oil, b. p. 200°/14 mm., of faint odour. The following condensation products were prepared by heating equivalent quantities of the constituents with acetic acid for about an hour: 5-benzylidene

derivative, $\begin{array}{c} CS-CH_2 \cdot CO \\ | \\ N(C_5H_{11}) \end{array} > C \cdot CHPh$, bright yellow needles, m. p.

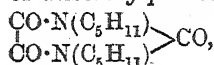
105°; 5-*o*-hydroxybenzylidene derivative, $C_{15}H_{17}O_3NS_2$, deep chrome-yellow needles, m. p. 175°; 5-*p*-hydroxybenzylidene derivative, deep yellow needles, m. p. 161°; 5-*p*-methoxybenzylidene derivative, $C_{16}H_{19}O_2NS_2$, pale chrome-yellow, prismatic needles, m. p. 116°; 5-*p*-nitrobenzylidene derivative, $C_{15}H_{16}O_3N_2S_2$, yellow, rhombic tablets, m. p. 163°; 5-*p*-dimethylaminobenzylidene derivative, carmine-red, crystalline scales, m. p. 154°; 5-*mp*-methylene-dioxybenzylidene derivative, $C_{16}H_{17}O_3NS_2$, yellow needles, m. p. 111°.

*iso*Amylthiocarbamide, when treated in alcoholic solution with cyanogen, is converted into the *imide* of *iso*amylothioparabanic acid, $\text{CS} \begin{array}{c} \text{N}(\text{C}_5\text{H}_{11}) \cdot \text{C} : \text{NH} \\ \text{NH} \text{---} \text{C} : \text{NH} \end{array}$, which, by warming with hydrochloric acid,

is hydrolysed to *iso*amylothioparabanic acid, $\begin{array}{c} \text{NH} \cdot \text{CS} \\ \text{CO} \cdot \text{CO} \end{array} > \text{N} \cdot \text{C}_5\text{H}_{11}$, yellow, silky needles, m. p. 125°; this on desulphurisation with silver nitrate in aqueous-alcoholic solution, yielded *iso*amytparabanic acid, $\begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{CO} \end{array} > \text{N} \cdot \text{C}_5\text{H}_{11}$, colourless, silky needles, m. p. 106°.

In a similar manner, phenyl*iso*amythiocarbamide, on treatment with cyanogen and subsequent hydrolysis, yielded phenyl*iso*amylothioparabanic acid, $\begin{array}{c} \text{NPh} \cdot \text{CS} \\ \text{CO} \cdot \text{CO} \end{array} > \text{N} \cdot \text{C}_5\text{H}_{11}$, fine, pale yellow needles, m. p. 94°, which when desulphurised gave phenyl*iso*amytparabanic acid, $\begin{array}{c} \text{NPh} \cdot \text{CO} \\ \text{CO} \cdot \text{CO} \end{array} > \text{N} \cdot \text{C}_5\text{H}_{11}$, fine, colourless needles, m. p. 85°.

*Diiso*amylothioparabanic acid, $\begin{array}{c} \text{CO} \cdot \text{N}(\text{C}_5\text{H}_{11}) \\ \text{CO} \cdot \text{N}(\text{C}_5\text{H}_{11}) \end{array} > \text{CS}$, prepared by hydrolysis of the additive compound of *diiso*amythiocarbamide and cyanogen, was converted by desulphurisation in the general manner, with formation of *diiso*amytparabanic acid,



both products being obtained as uncrystallisable syrups.

Di-p-hydroxyphenylthioparabanic acid, obtained by using di-*p*-hydroxyphenylthiocarbamide as starting point, formed yellow needles, which began to decompose near 360° without fusion, and on desulphurisation yielded colourless needles, m. p. above 360°.

*p-Tolyliso*amythiocarbamide, $\text{C}_5\text{H}_{11} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, needles, m. p. 217° (decomp.), was obtained by the action of *p*-toluidine on *iso*amythiocarbimide in alcoholic solution; by the usual series of chemical changes it was converted into *p-tolyliso*amylothioparabanic acid,

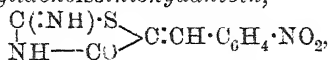
$\begin{array}{c} \text{CO} \text{---} \text{N}(\text{C}_5\text{H}_{11}) \\ \text{CO} \cdot \text{N}(\text{C}_6\text{H}_4\text{Me}) \end{array} > \text{CS}$, yellow needles, m. p. 111°, and *p-tolyl*-

*iso*amytparabanic acid, $\begin{array}{c} \text{CO} \text{---} \text{N}(\text{C}_5\text{H}_{11}) \\ \text{CO} \cdot \text{N}(\text{C}_6\text{H}_4\text{Me}) \end{array} > \text{CO}$, colourless needles, m. p. 90°.

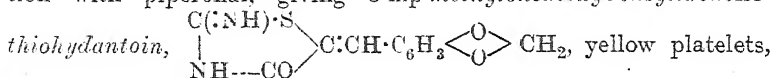
In order to examine the action of cyanogen on a trisubstituted thiocarbamide, phenyldiethylthiocarbamide was taken; the only isolable product was thiocarbamilide, the formation of which was probably due to the decomposition of some unstable intermediate product.

When *m*-nitrobenzaldehyde and "thiocarbimidoacetic" acid were mixed into a paste with the gradual addition of sodium hydroxide, condensation occurred, with formation of "*β*-*m*-nitrobenzylidene-thiocarbimidoacetic acid," $\begin{array}{c} \text{CO} \text{---} \text{S} \\ \text{NH} \cdot \text{CO} \end{array} > \text{C} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, pale yellow,

microscopic, rectangular plates, m. p. 277° (decomp.). Under similar conditions, thiohydantoin underwent condensation with *m*-nitrobenzaldehyde, giving β -*m*-nitrobenzylidenethiohydantoinic acid, $\text{NH}_2\cdot\text{C}(\text{:NH})\cdot\text{S}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, a colourless, crystalline solid, which, when recrystallised from acetic acid, was converted into β -*m*-nitrobenzylidenethiohydantoin,



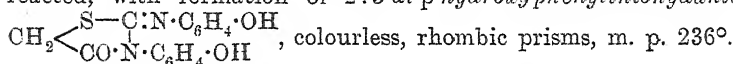
yellow needles, m. p. 260° ; the conversion of the former product into the latter also could be effected by heating to 200° . In a similar manner, thiohydantoin could be made to undergo condensation with piperonal, giving β -*mp*-methylenedioxybenzylidenethiohydantoin,



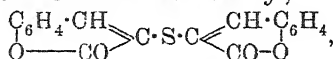
decomp. near 215° .

The method applied above for the condensation of aldehydes with thiohydantoin can be successfully substituted by heating the reagents with acetic acid and sodium acetate; thus, benzaldehyde and thiohydantoin under the latter conditions gave rise to β -benzylidenethiohydantoin, which has already been prepared by condensation in the presence of alkali (Kučera, A., 1914, i, 434).

When molecular quantities of di-*p*-hydroxyphenylthiocarbamide and chloroacetic acid were gently heated together, the substances reacted, with formation of 2:3-di-*p*-hydroxyphenylthiohydantoin,



Attempts to produce condensation products of thiodiglycollic acid with other aldehydes than benzaldehyde (Loven, A., 1885, 241) were fruitless except with salicylaldehyde, which in solution in boiling acetic acid in the presence of sodium acetate and acetic anhydride gave rise to 3:3'-thiodicumarinyl,



very pale yellow needles, m. p. $288-289^{\circ}$.

*iso*Amylthiocarbimide can be readily prepared by the action of ethyl chlorocarbonate on potassium *iso*amyldithiocarbamate, which is obtained by mixing *iso*amylamine, carbon disulphide, and potassium hydroxide in molecular proportion in alcoholic solution.

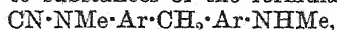
In a footnote by R. Andreasch, it is reasserted that the compound obtained by desulphurisation of ethylthioparabanic acid (A., 1898, i, 243) was in reality ethylparabanic acid (compare Biltz and Topp, A., 1913, i, 600).

D. F. T.

Partial Hydrolysis of Biscyanamides. J. VON BRAUN (*Ber.*, 1916, 49, 2600—2605).—The author has succeeded in finding the conditions under which compounds of the type

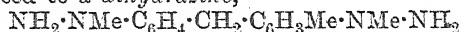


can be hydrolysed to substances of the formula



which may prove to be of interest for further investigations. This partial hydrolysis is effected by concentrated hydrochloric acid at temperatures just below 100° , whereas the boiling acid causes complete hydrolysis.

pp'-Dicyanodimethyldiaminodiphenylmethane is hydrolysed to *pp'*-dimethyldiaminodiphenylmethane by boiling hydrochloric acid (A., 1904, i, 687) or to *p*-methylamino-*p'*-cyanomethylaminodiphenylmethane, m. p. 112° , as indicated. This forms a sparingly soluble hydrochloride and a pale yellow nitroso-compound, m. p. 121° . *pp'*-Dicyanodimethyldiaminodi-*o*-tolylmethane yields either *pp'*-dimethyldiaminodi-*o*-tolylmethane, leaflets, m. p. $81-82^{\circ}$, which forms a *platinichloride*, decomp. 220° , a *benzoyl* derivative, m. p. 118° , a *phenylthiocarbamide*, m. p. 171° , and a *dinitroso*-compound, yellow leaflets, m. p. $105-106^{\circ}$, or *p*-methylamino-*p'*-cyanomethylaminodi-*o*-tolylmethane, m. p. $89-90^{\circ}$, which gives a yellow nitroso-compound, m. p. $93-94^{\circ}$. 2:4'-Dicyanodimethyldiaminophenyl-*m*-tolylmethane forms 2:4'-dimethyldiaminophenyl-*m*-tolylmethane, m. p. 57° , which yields a *diacetyl* compound, m. p. 124° , and a *dinitroso*-compound, m. p. 101° . This may be reduced to a *dihydrazine*,



m. p. $104-105^{\circ}$, which does not, apparently, condense with ketones, but gives crystalline hydrazones with many aldehydes (for example, derivatives of formaldehyde, m. p. 140° ; heptaldehyde, m. p. 54° ; benzaldehyde, m. p. 220° ; arabinose, m. p. 165° ; galactose, m. p. 180° ; rhamnose, m. p. 159°). Partial hydrolysis of the same bis-cyanamide apparently affects the group in the para-position; 2-cyanomethylaminophenyl-4-methylamino-*m*-tolylmethane has m. p. $111-112^{\circ}$, and forms a *picrate*, m. p. 173° , a *benzoyl* derivative, m. p. 100° , and a nitroso-compound, glistening, yellow leaflets, m. p. 105° .

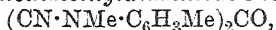
J. C. W.

***tert.*-Aminobenzyl Alcohols and their Derivatives. V. Basic Derivatives of Benzophenone.** J. VON BRAUN (*Ber.*, 1916, 49, 2605-2608).—Although *pp'*-tetramethyldiaminodiphenylmethane can be readily oxidised by chloranil to Michler's ketone (Kliegl, A., 1906, i, 433), such is not the case with other basic diphenylmethane derivatives in which one at least of the positions adjacent to the methylene bridge is occupied by a hindering group, such as the methyl or dimethylamino-groups. These compounds can, however, be converted into the benzophenones, the unsymmetrical ones having considerable interest, by the method developed in the cases of tetramethyldiaminodiphenylmethane (A., 1904, i, 687) and tetramethyldiaminoxanthen (A., 1916, i, 663).

Thus 2:4'-tetramethyldiaminophenyl-*m*-tolylmethane is converted into the dicyanodimethyldiamine, and this is oxidised by chromic acid to 2:4'-dicyanodimethyldiaminophenyl-*m*-tolyl ketone, $\text{CN} \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NMe} \cdot \text{CN}$, which crystallises in felted needles, m. p. 237° , and forms an *oxime*, m. p. 177° . The ketone is hydrolysed by boiling with concentrated hydrochloric acid to 2:4'-dimethyldiaminophenyl-*m*-tolyl ketone, a bright,

yellowish-green powder, m. p. 133°, which forms a pale yellow *platinichloride*, decomp. 290°, a *benzoyl* derivative, m. p. 202°, and a pale yellow *dinitroso*-compound, m. p. 221°, and may be converted by means of methyl iodide into the desired 2:4'-*tetramethyldiaminophenyl m-tolyl ketone*, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NMe}_2$, in leaflets, m. p. 143—144°.

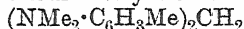
Similarly, *pp'*-*tetramethyldiaminodi-o-tolylmethane* can be converted into *pp'*-*dicyanodimethyldiaminodi-o-tolyl ketone*,



needles, m. p. 160°, and this into *pp'*-*dimethyldiaminodi-o-tolyl ketone*, m. p. 62—63°, which forms a pale yellow *dinitroso*-compound, m. p. 102°.

J. C. W.

***tert.*-Aminobenzyl Alcohols and their Derivatives. VI. Trioxymethylene and Dimethyl-*o*-toluidine.** J. VON BRAUN and K. HEIDER (*Ber.*, 1916, **49**, 2608—2610).—In 1892, Alexander heated some dimethyl-*o*-toluidine with trioxymethylene and dilute zinc chloride solution in sealed tubes at 170—180° for several hours, and obtained a non-volatile base which he supposed had the formula $(\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2)_2\text{CH}_2$. The authors have re-examined this subject, and find that the only non-volatile base (25% yield) is 4:4'-*tetramethyldiaminodi-m-tolylmethane*,



(*A.*, 1913, i, 1327).

J. C. W.

Ethylene Dibromide and Dimethylaniline. J. VON BRAUN and Z. ARKUSZEWSKI (*Ber.*, 1916, **49**, 2610—2612).—Schoop (*A.*, 1881, 160) obtained a non-volatile base by warming together dimethylaniline and ethylene dibromide, and this is still regarded as *pp'*-*tetramethyldiaminodiphenylethane*. It is now shown, however, that the base is really Fröhlich's ethylenedi-methylaniline [diphenyldimethylethylenediamine] (*A.*, 1907, i, 347). Apparently, a quaternary bromide is first formed, which then parts with methyl bromide, thus: $2\text{C}_6\text{H}_5 \cdot \text{NMe}_2 + \text{C}_2\text{H}_4\text{Br}_2 = (\text{Br} \cdot \text{NMe}_2\text{Ph})_2\text{C}_2\text{H}_4 = (\text{NMePh})_2\text{C}_2\text{H}_4 + 2\text{MeBr}$.

Characteristic of this diphenyldimethylethylenediamine, and the similar tri-, tetra-, and penta-methylene compounds, is the fact that they are readily oxidised by traces of many oxidising agents to very highly coloured (greenish-blue to reddish-blue) substances, which are receiving further attention.

J. C. W.

Constitution of Isatide. MORITZ KOHN (*Ber.*, 1916, **49**, 2514—2515. Compare Heller, *A.*, 1916, i, 753).—Kohn does not recognise in Heller's arguments in favour of a quinhydrone formulation for isatide any reasons for abandoning his pinacone formula.

J. C. W.

Some α -Styrylbenziminazoles and their Azo-dye Derivatives. O. KYM and S. JURKOWSKI (*Ber.*, 1916, **49**, 2681—2697).—In a number of papers since 1899, Kym has referred to the influence of various substituents on the colour of

2-phenylbenziminazoles and azo-dyes derived from them. It is now shown that corresponding styryl compounds are decidedly deeper in colour, and that amino- and nitro-derivatives of 2-styrylbenziminazole will even dye cotton fibres directly, to a certain extent. The styryl derivatives are readily obtained by the condensation of aldehydes with 5-nitro-2-methylbenziminazole, which is conveniently prepared by heating *p*-nitro-*o*-phenylenediamine with acetic anhydride and hydrolysing the acetyl compound so formed.

5-Nitro-2-styrylbenziminazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \text{C} \cdot \text{CH} \cdot \text{CHPh}$, is obtained by condensation with benzaldehyde, in golden-yellow needles, m. p. 90—95°, or by boiling *p*-nitro-*o*-phenylenediamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NH} \cdot \text{CO} \cdot \text{CH} \cdot \text{CHPh})_2$ (bulky, silver-white needles, m. p. 250—251°), with aqueous-alcoholic sodium hydroxide. This is reduced by tin and hydrochloric acid to 5-amino-2-styrylbenziminazole, which crystallises in bundles of pale yellow needles, m. p. 195—200°, and exhibits in alcoholic solution the intense pale green fluorescence characteristic of aminobenziminazoles. The 5-acetyl-amino-compound forms slender needles, m. p. 233°, and exhibits pale bluish-violet fluorescence.

5-Nitro-2-*p*-nitrostyrylbenziminazole, obtained by heating with the aldehyde at 180—210°, crystallises in deep yellow needles, m. p. above 300°, and forms a cinnabar-red sodium salt and a pale yellow hydrochloride. 5-Amino-2-*p*-aminostyrylbenziminazole forms heavy, sandy, yellow crystals, m. p. 237—238°, and dissolves in acids or sodium hydroxide.

Comparative tests were made on the tinctorial properties of the azo-dyes obtained by coupling the above amines with diazotised 2-naphthol-3:6-disulphonic acid (R) and 8-amino-1-naphthol-3:6-disulphonic acid (H) (see D.R.P., 288190, of 1914). The dyeing of cotton directly by all of the above derivatives in alkaline baths is also described.

5-Nitro-2-*p*-hydroxystyrylbenziminazole crystallises in orange-red flocks, m. p. above 300°; 5-nitro-2-*mp*-dihydroxystyrylbenziminazole forms brownish-yellow flocks, m. p. 271°; 5-nitro-2-*m*-hydroxy-*p*-methoxystyrylbenziminazole also forms orange-coloured flocks, m. p. 278—279°. Isatin also gives a condensation product,

$\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \text{C} \cdot \text{CH} \cdot \text{C} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix}$, in small, cinnabar-red, glistening crystals, m. p. above 300°, but phenanthraquinone forms an abnormal, dark green product, m. p. 256—258°. J. C. W.

The Hydrolysis of Methyl-*tert*-butyl- and Dimethyl-*tert*-butyl-triaminobenzene. J. HERZIG and F. WENZEL (*Monatsh.*, 1917, 37, 567—585).—Although 2:4:6-trinitro-1-methyl-3-*tert*-butylbenzene can be easily reduced to the corresponding amino-compound, the further conversion of this product into the corresponding substituted phloroglucinol is rendered difficult

by the tendency of the tertiary butyl radicle to undergo scission from the compound.

[With E. TAIGNER.]—Commercial trinitromethylbutylbenzene, after purification by recrystallisation, was reduced with tin and hydrochloric acid to 2:4:6-triamino-1-methyl-3-*tert.*-butylbenzene hydrochloride, $C_4H_9 \cdot C_6HMe(NH_2)_3 \cdot 3HCl$, colourless needles, which rapidly undergoes atmospheric oxidation, and gives a deep red coloration with ferric chloride solution. When warmed with acetic anhydride, the amino-compound was acetylated, with scission of one amino-group, the product being *diacetyldiaminoacetoxy-1-methyl-3-tert.-butylbenzene*, $C_4H_9 \cdot C_6HMe(NHAc)_2 \cdot OAc$, colourless, granular crystals, m. p. 268—270°, which on hydrolysis with hydrochloric acid yielded *diaminohydroxy-1-methyl-3-tert.-butylbenzene*, $C_4H_9 \cdot C_6HMe(NH_2)_2 \cdot OH$ (*dihydrochloride*, colourless needles, decomp. near 315°); this hydrochloride, when heated in boiling water in an atmosphere of carbon dioxide for several hours, underwent hydrolysis, with formation of methylphloroglucinol, the *tert.*-butyl group having been eliminated. Methylphloroglucinol was found to yield a triacetyl derivative capable of existence in two forms, m. p. 52° and 76° respectively (compare Weidel, A., 1898, i, 578).

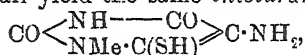
[With A. KICHLER.]—2:4:6-Trinitro-1:3-dimethyl-5-*tert.*-butylbenzene, when reduced with tin and hydrochloric acid, suffers partial loss of the butyl radicle, *diaminohydroxy-m-xylene dihydrochloride*, $OH \cdot C_6HMe_2(NH_2)_2 \cdot 2HCl$, needles [*penta-acetyl* derivative, $OAc \cdot C_6HMe_2(NAc)_2$, colourless crystals, m. p. 122—123°], and *triamino-m-xylene trihydrochloride*, $C_6HMe_2(NH_2)_3 \cdot 3HCl$, colourless crystals [*hexa-acetyl* derivative, $C_6HMe_2(NAc)_3$, needles, m. p. 192—194°], accompanying the normal product, namely 2:4:6-triamino-1:3-dimethyl-5-*tert.*-butylbenzene trihydrochloride, $C_4H_9 \cdot C_6HMe_2(NH_2)_3 \cdot 3HCl$, colourless crystals; this substance, when hydrolysed by boiling with water in an atmosphere of carbon dioxide, behaved in an analogous manner to its lower homologue, giving dimethylphloroglucinol (Weidel and Wenzel, A., 1898, i, 579, 580), together with some *aminodihydroxy-m-xylene* [*tri-acetyl* derivative, $NHAc \cdot C_6HMe_2(OAc)_2$, rhombic crystals, m. p. 113—114°].

When eliminated in the above manner, it is probable that the *tert.*-butyl radicle forms trimethylcarbinol. D. F. T.

The Isomeric 3-Methyluric Acids. EINAR BILMANN and JOHANNE BJERRUM (*Ber.*, 1916, 49, 2515—2522).—A critical examination has been made of the crystalline form, absorption spectra, solubility, and acid strength of the α -, δ -, and ζ -forms of 3-methyluric acid. In agreement with Fischer and Ach (1899), it is found that the α -acid, which is best prepared by Grohmann's method (A., 1911, i, 691), certainly differs in outward appearance from the δ -acid (Loeben, 1897) and the ζ -acid (Fischer and Ach), which are crystallographically identical. The three acids give almost exactly the same absorption curves for ultra-violet light as uric acid itself, so they can scarcely differ in any profound struc-

tural way. The H-ion concentration of 27.5×10^{-5} molar solutions of the α -, δ -, and ζ -acids was found by a colorimetric method to be 0.22×10^{-5} for the first and slightly less than 0.11×10^{-5} for the others, whilst the resistances of the same solutions in a certain apparatus were 20,670, 29,967, and 29,654 ohms respectively, that of uric acid of the same concentration being 19,080 ohms. The solubilities of the acids in water at 25° are 0.0162, 0.0054, and 0.0055 gram per 100 grams of solution.

The only indication of a difference between the δ - and ζ -acids is the fact that the latter is more readily attacked than the former (or the α -acid) by phosphoryl chloride (Fischer and Ach). Even if this should prove to be due to some hitherto unrecognised catalytic influence, there would still remain the difficulty of explaining the existence of two different 3-methyluric acids. The α - and δ -acids are certainly not polymorphic, for they crystallise separately from mixtures and cannot be changed one into the other by inoculation. They undoubtedly have the methyl groups in position 3, for they all yield the same *thioluramid*,



on heating with ammonium sulphide in a sealed tube (compare Fischer and Ach, A., 1896, i, 141). This compound forms elongated, straight-sided, colourless crystals, which are remarkably doubly refractive, the indices being 1.558 and 1.93. The α -acid, however, gives a poorer yield and reacts more sluggishly than the others.

J. C. W.

Diazo-compounds. XIV. Decomposition of Derivatives of Ethyl Diazoacetate by Heat. H. STAUDINGER and H. HIRZEL (*Ber.*, 1916, 49, 2522—2529. Compare A., 1916, i, 847—856).—Benzoylphenyldiazomethane decomposes on heating into diphenylketen (*ibid.*, 854). The action of heat on the diazoacylacetates and similar esters, which are readily formed by treating ethyl diazoacetate with acyl chlorides (*ibid.*, 855), has therefore been examined, in the hope of obtaining esters of keten-carboxylic acids. In most cases, however, substituted malonic esters are formed, but their production can be traced back to an inexplicable action of heat on the expected ketens. By carrying out the decomposition at as low a temperature as possible, for which boiling with xylene and some platinum chips usually serves, the intermediate ketens can, however, frequently be isolated.

Thus, if ethyl diazobenzoylacetate is heated alone at 250° , it yields ethyl phenylmalonate, but if the corresponding methyl ester is boiled with xylene as indicated, nitrogen is evolved quantitatively and the polymeride of the keten is left. When this is distilled, *methyl phenylketencarboxylate*, $\text{CO}:\text{CPh} \cdot \text{CO}_2\text{Me}$, is obtained as a lemon-yellow oil, b. p. $80\text{--}85^\circ/0.2$ mm. Similarly, ethyl diazoketosuccinate yields *ethyl ketendicarboxylate*, $\text{CO}:\text{C}(\text{CO}_2\text{Et})_2$, b. p. $115\text{--}116^\circ/11$ mm., mixed with much ethyl methanetricarboxylate, when heated carefully at 250° , but the almost pure keten when boiled with xylene.

Quantitative evolution of nitrogen was also realised in the decomposition of some other esters, including a thiodiazole derivative, but the products are not described as they are not the expected ketens.

J. C. W.

Action of Diazo-compounds on Copper Acetylide: Synthesis of Tetraphenylethane. V. V. SCHARVIN and N. I. PLACHUTA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 253—257).—According to Sandmeyer (A., 1884, 1311; 1885, 149), the interaction of copper acetylide and benzenediazonium chloride yields chlorobenzene, the action being a purely catalytic one brought about by the copper chloride resulting from the decomposition of the copper acetylide by the dilute acid; the acetylene, then, plays no part in the change. The authors' results show, however, that the acetylene does participate in the reaction, and that its carbon atoms enter into the hydrocarbon synthesised. In order to prevent the copper acetylide from floating on the surface of the liquid, the latter must be kept thoroughly mixed.

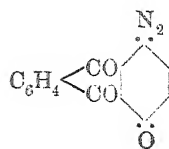
The action of benzenediazonium chloride (or *p*-nitrobenzenediazonium chloride) on copper acetylide yields a large proportion of chlorobenzene or *p*-chloronitrobenzene, and although other products are formed, chlorine is found in all the fractions distilled. With copper acetylide and benzenediazonium sulphate, the products obtained are: (1) a little phenol, (2) diphenyl, and (3) tetraphenylethane, the formation of which takes place according to the following equation: $4\text{N}:\text{NPh}\cdot\text{SO}_4\text{H} + 2\text{Cu}\cdot\text{C}\cdot\text{C}\cdot\text{Cu} = \text{CHPh}_2\cdot\text{CHPh}_2 + \text{C}_2\text{H}_2 + 4\text{N}_2 + 4\text{CuSO}_4$. The secondary reaction yielding diphenyl is expressed thus: $2\text{N}:\text{NPh}\cdot\text{SO}_4\text{H} + \text{Cu}\cdot\text{C}\cdot\text{C}\cdot\text{Cu} = \text{C}_6\text{H}_5\text{Ph} + \text{C}_2\text{H}_2 + 2\text{N}_2 + 2\text{CuSO}_4$.

In the case of silver acetylide and a diazonium salt, there is no reaction, neither marked evolution of gas, nor change in character of the precipitate, nor passage of the silver into solution occurring.

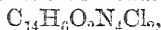
T. H. P.

Anthraquinone-1-diazonium Haloids. ALFRED SCHAAR-SCHMIDT (*Ber.*, 1916, **49**, 2678—2681).—*Anthraquinone-1-diazonium chloride* is remarkably stable, and can be obtained readily by diazotisation of a suspension of the pale grey hydrochloride of 1-aminoanthraquinone at 30—40°, and crystallisation from brine at 85—90°. It separates in pale brownish-yellow, glistening platelets. The golden-yellow *bromide* is formed by "salting-out" with potassium bromide; it will keep for weeks in a desiccator.

4-Chloroanthraquinone-1-diazonium chloride and *bromide* are even more stable. The former cannot be "salted-out," as it is too soluble; it is obtained by adding amyl nitrite to a suspension of the base in a mixture of glacial acetic acid and sufficient hydrochloric acid, and then diluting with ether. When warmed with dilute sodium acetate solution at 40—50°, it loses chlorine, and changes, apparently, into the *compound* (annexed formula), which



forms brownish-red needles. 1:4-Diaminoanthraquinone can be converted by the same means into anthraquinone-1:4-bis-diazonium chloride,



which forms bundles of pale brownish-red needles.

Anthraquinone-2-diazonium salts can be obtained in the same way. They are more unstable, and can be more easily converted into hydroxy-compounds, but they do not readily respond to Sandmeyer reactions. J. C. W.

Optical Activity of Albuminates of the Alkali Metals.

M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 265—268. Compare A., 1915, i, 1015).—Ammonium albuminate was prepared by treating a dilute aqueous albumin solution with ammonia and removing excess of the latter by evaporation to dryness. In order to prepare albuminates of the alkali metals, the dilute albumin solution is titrated with standard alkali hydroxide solution in presence of methyl-orange; equivalent proportions of the albumin and alkali solutions are then heated together at a temperature not exceeding 50°, the temperature of coagulation for a concentration of 1·5—3% being 56°. After careful evaporation of the solutions to dryness, the albuminates are treated with absolute alcohol to remove any possible trace of alkali. The albuminates prepared from non-coagulated albumin have the following specific rotations: ammonium, $-64\cdot51^\circ$, or, prepared in a sealed tube at about 50°, $-67\cdot56^\circ$; lithium, $-44\cdot87^\circ$; sodium, $-51\cdot09^\circ$; and potassium, $-55\cdot55^\circ$. Those prepared from coagulated albumin give the values: ammonium, $-56\cdot7^\circ$; lithium, $-48\cdot78^\circ$; sodium, $-52\cdot17^\circ$; and potassium, $-57\cdot09^\circ$. In this case, then, the ammonium compound has the highest rotation, whilst with the caseinogenates, glutinates, and nucleates the rotations increase in the order: lithium, ammonium, sodium, potassium. T. H. P.

Fibrin regarded as an Anisotropic, Amorphous, Solid Substance.

H. DIESSELHORST and H. FREUNDLICH (*Int. Zeitsch. physikal.-chem. Biol.*, 1916, **3**, 46—59).—The authors consider that fibrin belongs to the group of anisotropic, amorphous, solid substances which includes such substances as vanadium pentoxide. Hekma (A., 1914, i, 1013) has already shown that it forms sols and gels in which, on coagulation, particles are produced that, under the ultramicroscope, are seen to have a needle- or thread-like appearance. Many of the phenomena described by Hekma, such as the sudden appearance of fibrin needles after an incubation period and the growth of large needles by the fusion of amicronic particles, can be explained if the formation of fibrin is regarded as a coagulation with a subsequent growth of the coagulated particles, both reactions being of an autocatalytic nature and dependent on the kind and concentration of the coagulating agent. It is owing to the anisotropic, amorphous character of the fibrin particles that coagulation is aided by mechanical means, such as

stirring, which causes the fibrin needles to assume parallel positions, and thus enables them rapidly to join together to form fibres and threads.

H. W. B.

Optical Activity of Gelatinates of the Alkali Metals: Chemistry of α - and β -Gelatin. M. A. RAKUZIN and (MLLE.) EK. MAKS. BRAUDO (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 269—272).—Ammonium α -(or β -)gelatinates were prepared by the action of ammonia on a dilute (less than 0.75%) solution of gelatin (or β -gelatin), either in the cold or at the boiling point under the ordinary or increased pressure. The gelatin or β -gelatin solution was titrated with decinormal sodium hydroxide in presence of phenolphthalein, and the lithium, sodium, and potassium gelatinates prepared by boiling the gelatin or β -gelatin solution with the equivalent proportion of the corresponding hydroxide solution. The dry gelatinates were treated with absolute alcohol to remove any possible trace of free alkali. The specific rotations are as follows: α -Gelatin, -133.86° ; lithium α -gelatinates, -83.33° ; ammonium, -89.55° , or, when prepared under pressure, -100.00° ; sodium, -101.85° ; and potassium, -121.21° . β -Gelatin, -127.58° ; lithium β -gelatinates, -84.74° ; ammonium (prepared under pressure), -103.15° ; sodium, -106.55° ; potassium, -124.48° .

T. H. P.

Adsorption of Toxins and Antitoxins by Aluminium Hydroxide: Koch's Tuberculin. I. M. A. RAKUZIN and G. D. FLIER (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 711—716).—Of the eight ordinary colour reactions of the proteins, the only one not given by tuberculin is the violet coloration with fuming hydrochloric acid (Liebermann's reaction); since, further, tuberculin contains phosphorus, it must be regarded as an analogue of casein. In aqueous solution, its specific rotation is $[\alpha]_D -14.62^\circ$. By adsorption with aluminium hydroxide, it is separated into (1) 4.44% of an adsorbed antitoxin, which gives only Molisch's and Ostromisslenski's reactions, and in composition and properties resembles pepsin, the latter giving only Molisch's reaction; (2) 95.56% of a non-adsorbed toxin which, like casein, gives the biuret, Millon's, xanthoprotein, Adamkiewicz's, Molisch's, Pettenkofer's, and Ostromisslenski's reactions. The adsorption is irreversible.

T. H. P.

Optical Properties of Diastase and its Adsorption by Kaolin and by Aluminium Hydroxide. M. A. RAZUKIN and G. D. FLIER (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 321—324).—At 60° , only 84.12% of Merck's diastase is soluble in water; the solution is optically inactive, and gives the biuret, the xanthoprotein, Molisch's, and Ostromisslenski's reactions (compare A., 1915, ii, 602), the limits of sensitiveness being 1 in 1690, 840, 6660, and 750 respectively. In two diastase solutions, 7.19% and 7.10% of the total diastase present was adsorbed by aluminium hydroxide, and a second treatment with the latter effected no

further diminution in the specific gravity of the solution. Further, if the aluminium hydroxide is subsequently washed carefully and pressed, and then treated with hot water, the liquid shows none of the colour reactions of the original diastase solution; the adsorption is therefore irreversible. The adsorbed portion of the diastase fails to give Ostromisslenski's colour reaction with picramic acid. Since diastase consists of two enzymes, of which one converts starch into dextrins, whilst the other saccharifies it to maltose, it may be that the adsorbed and non-adsorbed parts correspond with these two constituents. Diastase is not adsorbed by the electronegative kaolin (compare Wo. Ostwald, "Grundriss der Kolloidchemie," 1909, 424).

T. H. P.

Intermediate Compounds in the Hydrolysis of Fats by the Lipase of Ricinus Seeds. N. V. TANCOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 257—264. Compare A., 1914, i, 759).—From the results of further experiments, the conclusion is drawn that the intermediate compounds formed by the lipase with the acid products of the hydrolysis of fats are least stable at the optimum concentration of the activator (sulphuric acid), the velocity of the reaction evidently depending on the velocity with which these compounds decompose in the solution. Both the substrate and the acid products of its hydrolysis accelerate the formation of the activator in mixtures of the seeds with water, in just the same way as the activator accelerates the scission of the substrate.

T. H. P.

Mode of Action of Urease and of Enzymes in General. K. GEORGE FALK (*J. Biol. Chem.*, 1917, 28, 389—390. Compare Van Slyke and Cullen, A., 1914, i, 1181, and succeeding abstract).—The author disputes the general validity of Van Slyke and Cullen's equation expressing the rate of enzyme action.

H. W. B.

Mode of Action of Urease and of Enzymes in General. DONALD D. VAN SLYKE and GLENN E. CULLEN (*J. Biol. Chem.*, 1917, 28, 391. Compare preceding abstract).—Polemical.

H. W. B.

Physiological Chemistry.

Elements which Condition the Activity of Glycolytic Enzymes. I. The Glycolytic Enzymes of the Pancreas, and Blood Corpuscles. UGO LOMBROSO (*Atti R. Accad. Lincei*, 1916, [v], 25, ii, 461—466).—When dextrose (about 1%) is dissolved in Tyrode's liquid and the solution circulated in the

pancreas and then placed in a thermostat, no diminution occurs in the proportion of dextrose present. Addition of blood corpuscles to the solution causes, however, a marked diminution in the reducing power, this being due, not merely to simple molecular condensation of the dextrose, but to its destruction. If the circulation in the pancreas is omitted, the content of dextrose in the liquid remains unchanged after blood corpuscles have been added. It is evident that, under the above experimental conditions, the pancreas emits a glycolytic enzyme into the circulating liquid, but that this enzyme manifests its maximal activity only with the aid of other factors, such as blood corpuscles. T. H. P.

Processes of Adsorption in Chemotherapeutics and Immunity. N. ANDREEV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 222—251).—As the majority of the constituent parts of the animal organism consist of colloids, the mechanism of many of the processes proceeding in it may be well explained from the point of view of the phenomena characteristic of disperse systems. Such explanations exist for metabolic changes, for the physiology of nutrition, for certain pathological phenomena, for the reaction between immune substances, etc., and the author extends them as forming the basis of chemotherapeutics and immunity.

In their relations to electrolytes and to cataphoresis, bacteria may be regarded as coarsely disperse of the suspensoid, emulsoid, or intermediate type with, in most cases, negative charges. Under the influence of an electric current, protozoa, like most amœbæ, exhibit positive charges. Since Ehrlich's arsenical preparations, containing arsenic as anion, have a therapeutic action on protozoa, but no curative effect on bacterial diseases, which are, however, influenced by preparations with poisonous cations, the conclusion is drawn that a process of electrical adsorption forms the foundation of chemotherapeutics. The ability of bacteria to change their charge under certain conditions allows of the application of Ehrlich's compounds to the cure of bacterial diseases.

That anti-substances may be regarded as globulins follows from the analogous relations of proteins and anti-toxins to physical and chemical factors, the ability of substances of both these types to adsorb irreversibly antigens, the high adsorptive power of serum proteins towards globulins, the precipitability of anti-substances from immune sera by globulins, and the absence of increase in the proteolytic enzymes in blood after injection of immune serum of an animal of the same kind.

The ability of proteins to decompose, yielding basic products which give rise to a specific anti-substance on immunisation, the formation of neutral compounds of toxins with acids, the rate of diffusion through gelatin, and the partial passage through animal membranes, justify the conclusion that toxins are products of the scission of proteins which are semi-colloidal in their physico-chemical relations. Evidence is adduced which indicates that mechanical adsorption, with its characteristic selectivity, forms the basis of specificity. T. H. P.

Influence of the Coagulation by Rennin on the Gastric Digestion of the Proteins of Milk. J. T. LEARY and S. H. SHEIB (*J. Biol. Chem.*, 1917, **28**, 393—398).—The proteins of milk are most easily digested by the gastric juice when the caseinogen has been previously precipitated by the addition of dilute hydrochloric acid to the whole milk. The addition of oxalate to the milk to prevent clotting is inadvisable, because the oxalate also slightly inhibits the action of the pepsin. The thick, elastic curd produced when milk curdles is only slowly attacked by gastric juice. Boiled milk is digested rather more quickly than unboiled milk.
H. W. B.

Comparative Biochemistry of Purine Metabolism. III. The Presence of Allantoin in Mammalian Blood. ANDREW HUNTER (*J. Biol. Chem.*, 1917, **28**, 369—374).—Allantoin has been isolated by the author from the blood of the ox and the pig, and identified by its crystalline form and melting point. Traces of allantoin were also detected in the blood of the horse and the sheep, but not in human blood.
H. W. B.

Infant Feeding. The Chemical Changes produced by the Addition of Calcium Hydroxide to Milk. A. W. BOSWORTH and H. I. BOWDITCH (*J. Biol. Chem.*, 1917, **28**, 431—435).—The addition of calcium hydroxide to milk, which normally contains some insoluble calcium hydrogen phosphate (Van Slyke and Bosworth, *A.*, 1915, **i**, 192), results in the precipitation of more calcium phosphate, the insoluble phosphates under these conditions being a mixture of the di- and tri-calcium phosphates. The reaction of the milk-serum is also brought towards the neutral point, the alkalinity of the calcium hydroxide being neutralised by the formation of the insoluble phosphates.

When applied to infant feeding, the milk is usually treated with lime water, and then diluted with an equal bulk of water. In these circumstances, owing to the precipitation of calcium phosphate, the soluble calcium and phosphorus in the diluted milk may be reduced to amounts less than those which are present in human milk.
H. W. B.

Effects of Feeding the Proteins of the Wheat Kernel at Different Planes of Intake. E. V. MCCOLLUM, N. SIMMONDS, and W. PITZ (*J. Biol. Chem.*, 1916, **28**, 211—229. Compare Hart, Miller, and McCollum, *A.*, 1916, **i**, 581).—Feeding experiments on rats confirm the conclusions previously drawn from the results obtained from wheat-fed pigs. A diet containing a relatively large proportion of wheat is injurious, not to the animals themselves, but to their offspring. Normal growth may be secured on a diet containing from 6% up to 40% of wheat protein, but either reproduction does not occur, or the young invariably die within a few days of birth. The results are illustrated by numerous charts.
H. W. B.

Is Lysine the Limiting Amino-acid in the Proteins of Wheat, Maize, or Oats? E. V. MCCOLLUM, N. SIMMONDS, and W. FITZ (*J. Biol. Chem.*, 1917, **28**, 483—499).—Rats are fed on wheat, maize, or oats as the sole source of protein, together with inorganic salts and butter fat, so that the diet is capable of promoting growth and general well-being, but the protein is too low in amount to enable growth to occur at the normal rate. The diets are then supplemented with either zein, which lacks tryptophan and lysine, or gelatin, which contains 6% of lysine, but neither tyrosine nor tryptophan. It is found that neither zein nor gelatin can sufficiently supplement the proteins of maize, so that the failure of maize adequately to promote growth is not due to a lack of lysine. On the other hand, gelatin added to either wheat or oats greatly improves its growth-promoting properties, whereas zein exerts a beneficial influence when combined with oats, but does not render wheat more efficient for the promotion of growth. It is possible, therefore, that lack of sufficient lysine accounts for the inadequacy of wheat protein, but in the case of oats, neither lysine, tyrosine, nor tryptophan can be the limiting amino-acid, of which the minimal amount present determines the abnormally low rate of growth.

H. W. B.

Mechanism of Cytolysis in Sea-urchin Eggs. A. R. MOORE (*J. Biol. Chem.*, 1917, **28**, 475—482).—The cytolysis of the fresh, unfertilised eggs of the sea-urchin by hot water can be represented as a process proceeding at the rate of a unimolecular reaction. Since strontium ions are found to act as a positive catalyst of this reaction, it is probable that the action of strontium ions in sensitising sea-urchin eggs to foreign sera and to starfish sperm is also due to catalysis of the cytolysis reaction.

H. W. B.

Proteins of the Central Nervous System. H. M. MCGREGOR (*J. Biol. Chem.*, 1917, **28**, 403—427).—The nervous tissue (sheep's brain) is dried in thin layers in a vacuum at 0°, and is then extracted with a mixture of benzene and alcohol, which extracts about 45% of the dry tissue. About 10% of the dry, fat-free residue consists of a *protein* containing iron and 0.11% of phosphorus. It is soluble in water, and is characterised by its instability. In the presence of weak acids, it is decomposed into at least three products, the natures of which are dependent on the nature and concentration of the acid employed. The protein obtained by different methods invariably contains iron.

A second *protein* is extracted from the dry, fat-free nervous tissue by dilute alkali hydroxide solutions. It also contains iron and 0.6% of phosphorus, and is present to the extent of approximately 10% of the dry tissue. It differs in properties from the protein extracted by water, and is precipitated completely by the addition of acid without decomposition.

The supporting tissue is insoluble in neutral, acid, or alkaline solvents, and consists, presumably, of a neurokeratin or sclero-protein. It comprises 20% of the dry tissue.

The brains of the ox, rabbit, sheep, dog, and man contain similar proteins. The same distribution of similar proteins occurs in each portion of the brain, namely, in the cerebrum, cerebellum, medulla, and pons of sheep's brain.

H. W. B.

Metabolism of Dextrose in Surviving Organs. II.
Action of the Pancreas on Dextrose Circulating in it.

CAMILLO ARTOM (*Atti R. Accad. Lincei*, 1916, [v], 25, ii, 466—471. Compare Lombroso, this vol., i, 102).—When blood containing dextrose is circulated in the pancreas of the dog, its reducing power always undergoes a diminution, which varies in amount in different cases, and may reach about 50%. The proportion of carbohydrates in the pancreas itself usually increases, but the amount of the increase is never greater than corresponds with about 55% of the quantity of dextrose disappearing from the blood. Tyrode's solution containing dextrose also loses in reducing power when circulated through the pancreas, but the loss is always less than with blood, and never exceeds 24%; a large part, sometimes more than 85%, of this loss is accounted for by increase in the proportion of carbohydrates in the pancreas. The behaviour of the pancreas in these two cases is in accord with that of the intestine. That more variable results are obtained with the pancreas is explained by the difficulty of maintaining the cellular elements in a state of functional integrity under artificial experimental conditions. The glycolytic activity of the pancreatic tissue becomes greater as the conditions employed approach more nearly to those in which the tissue exists in the living organism.

T. H. P.

Metabolism of Dextrose in Surviving Organs. III.
Action of the Spleen on Dextrose Circulating in it.

CAMILLO ARTOM (*Atti R. Accad. Lincei*, 1916, [v], 25, ii, 513—516).—When blood containing dextrose is circulated in dog's spleen, the reducing power of the blood is diminished to an extent which varies in different cases, and may amount to 25%. At the same time, the carbohydrate content of the spleen increases, but such increase never accounts for more than 70% of the dextrose which disappears from the blood. With Tyrode's solution containing dextrose, a similar diminution in the reducing power occurs during circulation in the spleen, such diminution being greater than the simultaneous increase in the amount of carbohydrates in the spleen itself.

T. H. P.

The Normal Content of Arsenic in Urine. PETER KLASON (*Arkiv Kem. Min. Geol.*, 1916, 6, No. 6, 1—6).—In a previous paper (A., 1915, ii, 649), the author has described a method for the oxidation, by means of nitric acid, of organic liquids containing arsenic. An improved form of apparatus is now described, and full details are given of the manipulation necessary for the estimation of the arsenic content of urine.

The author has never taken arsenic in any form, nor has he suffered from "arsenic sickness"; nevertheless, from investigations made on himself, he finds that the urine always contains arsenic to the extent of 0.005—0.0125 mg. per litre. He draws the conclusion that arsenic is a normal constituent of the human body, and consequently its use as a medicine (compare iron) can be understood. It is probably introduced in the food taken, and in much greater quantity than could come from wallpapers, carpets, clothing, etc.

It is stated that the methods which have hitherto been used for the estimation of arsenic in organic secretions are so inexact that the results obtained are worthless.

T. S. P.

Localisation of the Processes of Oxidation in the Cell and the Modifications Induced by Combinations of Electrolytes. VICTOR SCHLÄPFER (*Int. Zeitsch. physikal.-chem. Biol.*, 1916, 3, 1—45).—In general, a definite relationship exists between the weight of a rabbit and the amount of a dye which it is capable of receiving without the production of toxic effects. To account for this fact, the theory is advanced that the reducing power of living tissue is limited, being in the full-grown animal equivalent to 0.025 gram of dye per kilo. of tissue, whilst it is the unreduced dye which exerts the toxic action. Hence the amount of a dye which can be injected into an animal without the production of toxic effects is a measure of the oxidation occurring at the expense of the dye in the living tissue of the animal. It is further found that less reduction occurs when the animal is in a feverish condition; extirpation of the kidneys, testes, thyroid, and parathyroid glands in each case produces a similar effect. The inhibition of the processes of oxidation observed after these operations can also be produced by the simple injection of a solution of an ammonium salt. On the contrary, the introduction of salts of sodium or lithium accelerates the processes of oxidation in the cell, and, after any of the above operations, prevents the appearance of toxic symptoms after the injection of small quantities of a dye. In other words, those ions, sodium and lithium, which increase the excitability of muscle and nerve also stimulate the oxidation processes in the cell, whilst in each case the ammonium ion produces the reverse effect.

H. W. B.

Influence of Inositol on the Excretion of Phenol in the Dog. HARRY DUBIN (*J. Biol. Chem.*, 1917, 28, 429—430).—The ingestion of inositol does not lead to an increase in the amount of phenol excreted by the dog.

H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

The Loss in Alcoholic Fermentation. L. LINDET (*Compt. rend.*, 1917, **164**, 58—61).—If, in the fermentation of sugar, the yeast is supplied with an entirely mineral food containing ammonium sulphate, the loss of sugar is equal to about seventeen times the weight of yeast collected, two-thirds of the loss being in the form of carbon dioxide. If, however, to the solution other carbohydrates, such as gum arabic, rye-gum, or the humic substances of peat, are added to the extent of 2%, the fermentation becomes more rapid, the weight of yeast gathered is increased three times, and the ratio of loss of sugar to yeast gathered is only about one-third of that in the previous case. If a medium such as peptonised meat or gluten or yeast bouillon is used as a food supply for the yeast, the amount of yeast collected is about the same as in the previous case, but the loss of sugar per unit weight of yeast is much smaller. The sucrose is a poor nutrient for the yeast, ammonium salts in its presence only being with difficulty converted into protein. W. G.

Fermentation of Dibasic Acids. I. Malic Acid. A. LEBEDEV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 725—748).—In presence of yeast, malic acid is, to some extent, decomposed, with formation of lactic acid.

The separation and estimation of lactic acid in presence of malic acid by Kunz's method (A., 1901, ii, 700) gives quantitative results if 3 vols. of 96% alcohol instead of 2 vols. of 95% alcohol are added per 1 vol. of solution; further, this addition must be made in small portions and with constant shaking, since otherwise the barium lactate is partly precipitated.

Attention is directed to the presence in commercial ether of acetaldehyde, alcohol, acetic acid, etc., this being regarded as the source of the acetaldehyde detected by Buchner and Langheld (A., 1913, i, 944) in sugar solution fermented by means of yeast juice in presence of a phosphate.

Experiment shows that, in 2% concentration, malic acid is readily fermented by yeast, the decomposition it undergoes being, however, more profound than that represented by the equation $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H} = \text{CO}_2 + \text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$. When its concentration is 4%, malic acid is only feebly fermented, evidently owing to the high acidity of the solution.

All the results obtained show that the initial stage in the fermentation of malic acid consists in the scission of carboxyl from the group, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot$, this change being perfectly analogous to the breaking of the aldol linking. On this account, the author regards the carboxylase concerned, which is possibly not identical with the carboxylase of Neubauer and Neuberg, as belonging to the group of the aldolases. Such enzymes have not yet been

isolated, but undoubtedly exist, as is shown by the lactic and alcoholic fermentations of the hexoses, in which a chain of six carbon atoms is broken into two chains of three carbon atoms. It might be expected that many, if not all, dibasic acids containing the group $\text{CO}_2\text{H}\cdot\text{CH}_2$ would be decomposed by carboxylase, and the same might be expected of polybasic acids, since citric acid is also readily fermented by yeast. In the fermentation of succinic acid, the latter appears to decompose, first, into carbon dioxide and propionic acid, but with malonic acid no decomposition is effected by yeast. The action of carboxylase is therefore specific.

In presence of methylene-blue, the fermentation of malic acid gives rise to acetaldehyde. It is found also that, in presence of acetaldehyde, a comparatively small proportion of the lactic acid undergoes oxidation to pyrotartaric acid. The results show that, if lactic acid is fermented to alcohol and carbon dioxide, such reaction is extremely slow, and must be regarded as a secondary one. From the fact that malic acid is dehydrated more slowly and feebly than lactic acid, it is supposed that in the decomposition of malic acid, carbon dioxide is first split off, the lactic acid being dehydrated as it is formed.

T. H. P.

Investigation of the Influence of Climatic Conditions on the Composition of Plant Oils. G. V. PIGULEVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 324—341. Compare A., 1915, i, 758).—Evidence is adduced showing that, among plants belonging to one and the same sub-family, the iodine number of the essential oil increases as the geographical distribution of the plant extends further towards the north.

Plants of the families *Rosaceae*, *Ericaceae*, and *Pinaceae* yield oils containing the same acids. In the case of oleic acid, for which a number of isomerides are possible with different positions of the double linking, the natural acid is practically always the Δ^6 -acid, and the existence of this acid is doubtless related to its activity, since the activity varies considerably with the position of the double linking in the carbon chain.

The iodine number of an oil, characterising the degree of unsaturation, depends on the percentages of the triglycerides of unsaturated acids, and may be expressed by the formula

$$A_m = a_1x/100 + a_2y/100 + a_3z/100,$$

where A_m is the iodine number, x , y , and z are the percentages of the triglycerides of oleic, linoleic, and linolenic acids respectively, and a_1 , a_2 , and a_3 , the corresponding iodine numbers of the triglycerides, have the respective values 86.2, 173.58, and 262.15. By means of this formula, a table has been constructed which shows how, for one and the same iodine number, the proportions of the three triglycerides may vary.

T. H. P.

Humus Formation as an Essential Property of Plants.

A. TROUSSOV (*Bied. Zentr.*, 1916, 45, 434—435; from *Selskoie Khoziaistvo i Lesovodstvo*, Petrograd, 1914, 74, 233—246).—In a series of laboratory experiments, humus was obtained from various

organic compounds of vegetable origin by the action of acids and alkalis. The stages of the reaction are described as follows: Mono- and di-saccharides are first transformed into polysaccharides. Then, by a further loss of the elements of water, the molecules are broken down, and, after undergoing oxidation, finally yield humus. Where there is no oxidation, however, ulmin and ulmic acid are formed.

Humus is yielded by a mixture of aldehydes and polyhydric alcohols, but not by aldehydes alone, neither can it be obtained from pure ketones. The author considers that under natural conditions the stages are as described, but that micro-organisms take the place of acids and alkalis. Thus, the processes leading to humus formation consist of a perfectly definite series of chemical changes, and are not the result of an irregular destruction of molecules.

L. M. U.

Effects of Large Applications of Commercial Fertilisers on Carnations. GEORGE D. BEAL and FRED WEAVER MUNCIE (*J. Amer. Chem. Soc.*, 1916, **38**, 2784—2804).—The fertilisers used were dried blood, sodium nitrate, ammonium sulphate, calcium superphosphate, disodium hydrogen phosphate, and potassium sulphate, sodium chloride and sulphate being used for comparison. The carnation cuttings were grown on selected soil, uniform throughout the benches, the watering, heating, ventilation, and illumination being as nearly identical as possible in each section. Weekly applications of the fertilisers at various rates were given on isolated sections from October 1st to May 1st, or until injury became serious. The easily soluble fertilisers produced almost immediate injury, the moderately soluble delayed injury, the sparingly soluble producing no apparent injury. The botanical injuries characteristic of an excess of each fertiliser are recorded.

An increase in the dry weight and ash content of the foliage is obtained with an increased application of each fertiliser, there being an increased content of the fertilising salt in the plant after large application to the soil. There is an increased intake of nitrogen when ammonium sulphate is applied, but the plant acquires a tolerance when successive small doses are applied. Injury from ammonium sulphate is not proportional to the total nitrogen content. Osmotic pressure determinations made on the sap, expressed from the stems after freezing, proved that with each fertiliser used the degree of injury varied with the osmotic pressure, this injury for a given osmotic pressure varying with the fertiliser used. Increase in osmotic pressure is not the exclusive cause of the plant injury. This increase is accompanied by an increase in the total solids and ash of the sap and in the amount of fertiliser taken up by the plant. There is an increase in the total acidity of the sap of plants fed on ammonium sulphate, disodium hydrogen phosphate, and monocalcium phosphate, phenolphthalein being the indicator, but none with potassium sulphate. Plants grown on soil to which large applications of potassium sulphate had been made gave a sap showing a higher total sugar content, as did also

extracts of the foliage. The starch content of the foliage of such plants was lower. W. G.

Proteins from the Jack Bean, *Canavalia ensiformis*. D. BREESE JONES and CARL O. JOHNS (*J. Biol. Chem.*, 1916, **28**, 67—75. Compare A., 1916, i, 357).—The jack bean contains two globulins which can be separated by fractional precipitation with ammonium sulphate. One of them, *canavalin*, has the composition C 53·26, H 7·03, O 22·51, N 16·72, and S 0·48%, and the other, *concanavalin*, C 53·28, H 7·02, O 22·15, N 16·45, and S 1·10%. After the removal of the globulins, the extract of the jack bean still contains protein, which has been isolated and found to be an *albumin* of the legumelin type with the composition C 53·24, H 7·00, O 22·50, N 16·38, and S 0·88%. H. W. B.

Some Constituents of Jambul. MERRILL C. HART and FREDERICK W. HEYL (*J. Amer. Chem. Soc.*, 1916, **38**, 2805—2813).—An examination of the seeds of the Jambul tree (*Syzygium Jambolana*). The study of the resin gave, in general, the same results as those obtained by Power and Callan (compare A., 1912, ii, 480; 1913, i, 1057). The authors were able to obtain more conclusive evidence as to the presence, in the light petroleum extract, of myricyl alcohol, a hydrocarbon, probably hentriacontane, and of a phytosterol, $C_{27}H_{46}O$, m. p. 135—135·5°, giving an acetate, m. p. 119—120°. The ether and the chloroform extracts yielded a phytosterolin, m. p. 275—285°, giving an acetate, m. p. 167—168°. This was shown to be phytosterol *d*-glucoside. W. G.

Proteins of the Peanut, *Arachis hypogæa*. I. The Globulins Arachin and Conarachin. CARL O. JOHNS and D. BREESE JONES (*J. Biol. Chem.*, 1916, **28**, 77—87).—The peanut contains two globulins, *arachin*, C 52·15, H 6·93, O 22·23, N 18·29, S 0·40%, and *conarachin*, C 51·17, H 6·87, O 22·58, N 18·29, and S 1·09%. Conarachin contains 6·55% of basic nitrogen, which is the highest percentage of basic nitrogen recorded for any seed protein. Peanut press-cake may therefore prove to be highly effective in supplementing cattle-food products made from cereals and other seeds the proteins of which are deficient in basic amino-acids. H. W. B.

Saponin from *Yucca filamentosa*. L. H. CHERNOFF, ARNO VIEHOEVER, and CARL O. JOHNS (*J. Biol. Chem.*, 1917, **28**, 437—443).—The *saponin*, $C_{24}H_{40}O_{14}$, occurs as brown, amorphous masses in the fibrovascular bundles of the roots and leaf bases of *Yucca filamentosa*. It is obtained in the form of a white, amorphous powder by extraction of the dried roots with alcohol. On hydrolysis, it yields a *sapogenin*, crystallising in needles, m. p. 175°, together with dextrose and possibly glycuronic acid. Hæmolytic action was observed with the saponin, but not with the sapogenin. H. W. B.

The Characteristic Effect of Ammonium Salts on Plant Physiology. H. G. SÖDERBAUM (*Bied. Zentr.*, 1916, **45**, 454—455; from *Medd. No. 125 Centralanst. jordbruksförsök, Stockholm*, 1915, 13).—Phosphatic manures in the form of superphosphate, basic slag, and bone meal were applied to barley, with cross-dressings of sodium nitrate, ammonium sulphate, and ammonium chloride. Further, each plot was subdivided into three parts, two of which received magnesium salts (one the carbonate and the other the sulphate), whilst the third received no magnesium. The ammonium salts caused considerable depression of growth, especially when used with superphosphate, and to a less extent when used with bone meal. The leaves yellowed, and some plants died. With basic slag, however, the results were different; all plots were normal, as were all those which received magnesium carbonate; moreover, affected plots recovered rapidly with applications of magnesium carbonate, but not with magnesium sulphate. The author attributes the physiological disturbances of the plants not so much to any physiological acid reaction of the ammonium salts as to an actual toxic effect produced by them. L. M. U

Iodine Content of Food Materials. RALPH M. BOHN (*J. Biol. Chem.*, 1917, **28**, 375—381).—Most food materials used in cattle feeding, such as hay, straw, oil meal, rock salt, and well water, contain only a minute trace, if any, of iodine. Kendall's method (*A.*, 1914, ii, 815) was employed. H. W. B.

Efficiency of Certain Milk Substitutes in Calf Feeding. R. H. CARR, GEORGE SPITZER, R. E. CALDWELL, and O. H. ANDERSON (*J. Biol. Chem.*, 1917, **28**, 501—509).—The results indicate that various mixtures of animal and vegetable feeding materials are not as efficient as skim-milk for producing growth and development of the calf. H. W. B.

Dietary Deficiencies of the Maize Kernel. E. V. McCOLLUM, N. SIMMONDS, and W. PITZ (*J. Biol. Chem.*, 1916, **28**, 153—165. Compare Hart and McCollum, *A.*, 1915, i, 39).—The experiments with pigs have now been repeated with rats, using the proteins of maize as the sole source of protein in the food. The results indicate that the proteins of maize contain all the amino-acids essential for growth, and also both the accessory factors termed "fat-soluble A" and "water-soluble B." The fat-soluble A is, however, present in relatively too small a proportion for maximum rate of growth to occur in rats without the addition of substances relatively rich in this factor, such as butter or other fats. The inorganic content of maize is also not suitable for the promotion of growth, and it is therefore necessary to add various salts to the rations before growth can take place. Even when the diet is supplemented in the manner indicated, the physiological well-being of the animal is not maintained throughout life, and it is considered doubtful whether a completely satisfactory diet can be derived entirely from the maize kernel as the sole source of protein. H. W. B.

Organic Chemistry

The Thermal Decomposition of Low Temperature Coal Tar. DAVID TREVOR JONES (*J. Soc. Chem. Ind.*, 1917, 36, 3—7. Compare Jones and Wheeler, T., 1915, 107, 1318).—In an earlier paper (Jones and Wheeler, *loc. cit.*), an examination has been made of the nature of the tar obtained on distilling coal in a vacuum below 450°. The author has now investigated the thermal decomposition of this tar at temperatures between 550° and 800°, experiments being made by allowing the tar to flow over coke in a vertical tube of hard glass in an electric furnace, and also by distilling small quantities of the tar from a porcelain boat over porous porcelain in an atmosphere of carbon dioxide in a tube of hard glass or quartz.

As a result of the comparison of the composition of the distillate with that of the original tar and of the composition of the volatile product obtained at different temperatures, the following conclusions are drawn.

Ordinary coal-tar from coal at high temperatures is formed chiefly as the result of the decomposition of a tar previously formed at low temperature. The mechanism of the process consists essentially in the decomposition of the naphthenes, paraffins, and unsaturated hydrocarbons present in the low-temperature tar to form various olefines, which, at higher temperatures, condense to aromatic substances. The gaseous olefines of higher molecular weight are formed in maximum quantity at lower temperatures, their amount becoming negligible at 750°; this disappearance synchronises with the appearance of naphthalene, and immediately precedes a marked increase in the percentage of hydrogen. At medium temperatures, the formation of hydrogen is due to the decomposition of naphthenes, whilst the increase at higher temperatures is probably caused by the intermolecular and intramolecular condensation of aromatic compounds.

Phenols are primary products of coal distillation, but benzene and its homologues are produced in the secondary decomposition, chiefly as the result of olefinic condensation, but also, in part, by the thermal dehydrogenation of the corresponding naphthenes.

The part played by acetylene in coal-tar formation is insignificant (compare Meyer, A., 1912, i, 525). D. F. T.

Spinacene. A New Hydrocarbon from certain Fish Liver Oils. A. CHASTON CHAPMAN (T., 1917, 111, 56—69).—In the examination of a reputed cod-liver oil, a remarkably high proportion of unsaturated hydrocarbon oil was found to be present, amounting to 89% of the total weight. This result is not due to any adulteration of the oil, but to the extraction of oil from the livers of two species of fish, *Centrophorus granulosus* and *Scymnus lichia*; these are caught off the Moroccan coast, and have only

recently come into the Portuguese market (compare Mastbaum, *Chem. Zeit.*, 1915, **39**, 139, 889; Tsujimoto, A., 1916, i, 786).

From the unsaponifiable portion of the oil, an optically inactive liquid hydrocarbon, *spinacene*, $C_{30}H_{50}$, b. p. 268—269°/10 mm., D_{20}^{25} 0.8616, n_D^{20} 1.4967, was separated by distillation; this substance yielded a *hexahydrochloride*, a *trihydrochloride*, a *dodecaboride*, a *trinitrosochloride*, a *hexanitrosochloride*, and a *nitrosate*. The trinitrosochloride was further converted into a *dinitrosochloride mononitrolpiperidide*, a *trinitrolpiperidide*, a *dinitrosochloride mononitrolbenzylamide*, and a *trinitrolbenzylamide*. On hydrogenation, spinacene gave a saturated hydrocarbon, $C_{30}H_{62}$, b. p. 274—275°/18 mm., D_{20}^{25} 0.8172, n_D^{25} 1.4547.

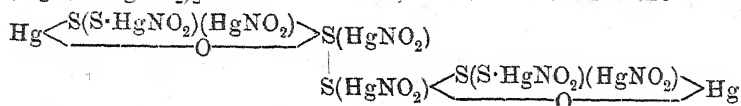
For experimental details see the original.

D. F. T.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. III. Chain Compounds and Sulphur.

PRAFULLA CHANDRA RÂY (T., 1917, **111**, 101—109. Compare A., 1916, i, 246, 542).—As thiocarbamide, thioacetamide, and thiobenzamide are capable of reacting in a tautomeric form as imino-mercaptans (Rây, T., 1914, **105**, 2159; A., 1916, i, 633), these compounds might be expected to react with mercuric nitrite; this anticipation has been realised, but the result is not quite as expected. Thus thiocarbamide and mercuric nitrite in aqueous solution yield a substance, $NH_2 \cdot C(:NH) \cdot S(HgNO_2) < \overset{Hg}{O}$, probably

formed by elimination of a molecule of nitrogen trioxide from an additive compound of the primary product, $NH_2 \cdot C(:NH) \cdot S \cdot HgNO_2$, with more mercuric nitrite. The former product is obtained only with certain precautions, the more usual product, which is formed exclusively when thioacetamide, thiobenzamide, and the thiocarbimides are submitted to the same reaction, being a compound $(HgO, 3SHgNO_2)_2$. This substance, to which the structure



is ascribed, reacts with methyl iodide, giving the disulphonium compound, Me_2S_2, HgI_2, MeI , and with ethyl iodide yielding *dimercuric di-iodosulphide*, $HgI \cdot S_2 \cdot HgI$, together with a compound, $SEt \cdot S \cdot SEt \cdot I \cdot HgI$, and a compound, Et_2S_2, HgI_2, EtI .

For details the original should be consulted.

D. F. T.

Preparation of Acetic Anhydride. H. DREYFUS (Brit. Pat., 17920, 1915; from *J. Soc. Chem. Ind.*, 1917, **36**, 162).—Acetic anhydride is prepared by acting on an acetate with sulphuric oxide (which may or may not be mixed with chlorosulphonic acid) or with a compound of sulphuric oxide with an inorganic salt, for example, sodium chloride or sulphate. A diluent, such as acetic anhydride, is used, and the reaction mixture must be cooled initially to 0—5° if sulphuric oxide is employed directly

or to atmospheric temperature by water cooling if a compound of sulphuric oxide is used. Thus, sulphuric oxide (800 kilos.) is added fairly rapidly, with constant stirring, to powdered anhydrous sodium sulphate (1600 kilos.), and when combination is complete the mass is cooled and added to a mixture of powdered anhydrous sodium acetate (1640 kilos.) and acetic anhydride (1600 kilos.), the mixture being stirred and water-cooled. The temperature may subsequently be allowed to rise to 60–70° to complete the reaction. The acetic anhydride is distilled under diminished pressure. The product is of a high degree of purity and free from chlorine. H. W.

Isomerism of Erucic, Brassidic, and *iso*Erucic Acids. Results obtained by the Cryohydrate or Eutectic Method. V. L. MASCARELLI (*Atti R. Accad. Lincei*, 1917, [v], 26, i, 71–74. Compare A., 1915, i, 863, 937).—These acids have been subjected to conditions analogous to those employed in Biilmann's experiments (A., 1909, i, 155, 382), but in no case could transformation of one acid into either of the other two be observed. A few experiments have also been made on the lines of those carried out by Stobbe and Schönburg (A., 1914, i, 173) on the cinnamic acids, but none of the three acids undergoes change on protracted storage or on separation from solution in various solvents.

The method given by Sidgwick (T., 1915, 107, 673), which had previously been suggested by Bruni (*Atti Accad. Sci. Padova*, 1910, 26, 357), has also been applied to the elucidation of the relations between the erucic acids. The results obtained show that erucic and brassidic acids are truly isomeric, this conclusion being in complete accord with the results of the author's previous work and with the mode of formation of the one acid from the other. Erucic and *iso*erucic acids also represent a case of true isomerism, but brassidic and *iso*erucic acids are more probably to be regarded as two forms of one and the same compound, that is, as dimorphous. T. H. P.

Alkaline Earth Oxalates. W. CECISNER DE CONINCK (*Ann. Chim. anal.*, 1917, 22, 23–24. Compare A., 1916, i, 369).—When very dilute barium nitrate solution is mixed with a slight excess of dilute oxalic acid solution, a precipitate of the trihydrate of barium oxalate, $2\text{BaC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, forms gradually within a period of about four weeks. Under similar conditions, calcium yields a mixture of mono- and di-hydrates, the latter predominating. Strontium hydrogen oxalate is obtained as the trihydrate, $\text{Sr}(\text{HC}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$, by treating concentrated strontium chloride solution with its own volume of concentrated hydrochloric acid and adding three volumes of saturated oxalic acid solution; this salt is decomposed by boiling water, with the formation of the normal salt, $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. W. P. S.

Influence of Aminoacetic Acid and α -Aminopropionic Acid on the Action of Alkali on Dextrose. H. I. WATERMAN (*Chem. Weekblad*, 1917, 14, 119–124).—Measurements of the

polarising power of dextrose solutions acted on by sodium hydroxide at 33° indicate that the presence of glycine or alanine retards the action.

A. J. W.

Organic Double Compounds of the Bismuth Haloids. L. VANINO and F. MUSSGUG (*Ber.*, 1917, 50, 21—24).—The bismuth haloids form well-crystallised, yellow or red additive compounds with thiocarbamides of the general type $\text{BiX}_3 \cdot 3\text{CS}(\text{NR}_2)_2$.

The yellow and red compounds of bismuth chloride with thiocarbamide, described by Hofmann and Gonder (*A.*, 1904, i, 231), are of the same composition, $\text{BiCl}_3 \cdot 3\text{CS}(\text{NH}_2)_2$. The yellow form melts at about 180° and the red at 186° , and the yellow substance changes into the red on drying. Other compounds obtained are as follows: $\text{BiCl}_3 \cdot 3\text{NH}_2 \cdot \text{CS} \cdot \text{NHPh}$, m. p. 157 — 158° ;

$\text{BiCl}_3 \cdot 3\text{NH}_2 \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}(o)$, yellow prisms, m. p. 185° ; $\text{BiBr}_3 \cdot 3\text{CS}(\text{NH}_2)_2$, m. p. 193° ; $\text{BiI}_3 \cdot 3\text{CS}(\text{NH}_2)_2$, cinnabar-red, m. p. 164 — 165° .

Trimethylsulphonium iodide gives a reddish-yellow compound, $\text{BiCl}_3 \cdot \text{SMe}_3\text{I}$, m. p. 228° , and phenyl mercaptan forms the compound, $\text{Bi}(\text{SPh})_3$, m. p. 98 — 99° .

Antimony trichloride combines with thiocarbamide to give a lemon-yellow compound, $\text{SbCl}_3 \cdot 3\text{CS}(\text{NH}_2)_2$.

J. C. W.

Preparation of Pharmaceutical Products containing Arsenic. SYNTHETIC PATENTS Co. (U.S. Pat., 1201692; from *J. Soc. Chem. Ind.*, 1917, 36, 162—163).—Compounds containing the following groups are claimed: $\text{RCX}:\text{CR}'\text{As}$, $\text{RCX}:\text{CR}'\text{As}$, $\text{RCX}:\text{CR}'\text{AsO}$, $\text{CRX}:\text{CR}'\text{AsO}(\text{OH})_2$, $\text{RCCl}:\text{CR}'\text{AsO}(\text{OH})_2$ (in which R or R' is hydrogen or a hydrocarbon radicle and X is a halogen), and, in particular, the chloroarsinic acids produced by causing arsenic trichloride to combine with hydrocarbons of the acetylene series, treating the product with water to form the arsenoxide and oxidising the latter. Thus, Δ^7 -heptinene (240 parts) is heated under reflux with arsenic trichloride (900 parts) for sixteen hours; excess of arsenic trichloride is removed by distillation in a vacuum, and the oily residue is dissolved in wet ether (3000 parts). Aniline is added as long as a precipitate forms, and the aniline hydrochloride is removed. The filtrate is washed with dilute hydrochloric acid, then with water until neutral to Congo-red, dried over sodium sulphate, and freed from ether in a vacuum. *Chloroheptinenearsen oxide* remains as a viscous, dark liquid, 44 parts of which are dissolved in acetone (400 parts) and treated with hydrogen peroxide (3%) until oxidation is complete. The solution is shaken with ether (500 parts), and the ethereal layer washed with dilute sodium hydroxide and water. The alkaline wash-water is acidified with hydrochloric acid and concentrated in a vacuum at 60 — 70° until the *chloroheptinenearsinic acid* crystallises. It is separated, washed with a little ether, decolorised with animal charcoal, and crystallised. It forms white, shining leaflets, readily soluble in water to a neutral solution, and is valuable in the treatment of anæmia, chlorosis, leucæmia, chorea, and skin diseases.

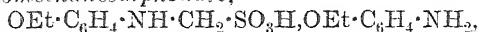
H. W.

Preparation of Monoalkylated Aromatic Amines (*N*-Alkyl-arylamines). G. T. MORGAN (Brit. Pat., 102834; from *J. Soc. Chem. Ind.*, 1917, **36**, 207—208).—*N*-Alkylarylamines are prepared from aniline or naphthylamines or their homologues or simple substitution products (other than nitro-compounds) by treating the amine with an aliphatic aldehyde in the presence of a reducing agent in a medium not possessing a strongly acid character. The anhydroaldehyde-amine, or Schiff base, produced from the amine and aldehyde, is simultaneously reduced to the alkylaromatic amine. Thus, aniline (60 parts) and formaldehyde (40%, 66 parts) are added slowly and concurrently to a solution of sodium hydroxide (34%, D 1.37, 300 parts) containing zinc dust (90 parts) in suspension. The addition of the reagents should occupy about two hours, and the mixture should be well stirred and kept at 90°. The heating and stirring are continued for six hours longer, during which formaldehyde (40%, 40 parts) is slowly added. When the percentage of methylaniline has reached a maximum, the mixture is steam distilled, and the methylaniline isolated from the distillate in any of the usual ways. H. W.

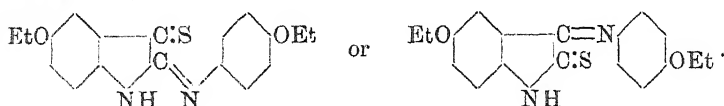
Electrolytic Preparation of Aromatic Amino-hydroxy-compounds. SOC. CHIM. IND., BASLE (Brit. Pat., 18081, 1915; from *J. Soc. Chem. Ind.*, 1917, **36**, 129).—In the electrolytic reduction of aromatic nitro-compounds, the formation of aminohydroxy-compounds is favoured and that of amine reduced by the use of a cathode of two or more metals. The cathode is obtained either by use of a suitable alloy, the surface of which remains practically constant in composition during the reaction, or by making the cathode of one metal and placing the other, either as such or as salt, in the electrolyte, or by using an indifferent substance, such as carbon, and depositing the metal thereon during electrolysis. It is possible to reduce the amount of acid to very little more than that necessary to combine with the base which is formed. Details are given of the reduction of nitrobenzene, using a copper cathode with lead, or lead and arsenic, in the solution, and with a lead cathode with bismuth in the electrolyte. Other suitable combinations of metals are copper with mercury and copper with tin and arsenic. A plain lead cathode under these conditions would give *p*-aminophenol and aniline in the proportion of about 2 to 3, whilst this method gives them in the proportion of 5 or 6 to 1. H. W.

Certain Products of the Action of Formaldehyde and a Hydrogen Sulphite on Aromatic Amines and their Derivatives. I. ROBERTO LEPETIT (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 126—132).—Sodium *p*-phenetidinomethanesulphonate (nevraltine) (compare A., 1909, i, 569) decomposes and turns yellow at about 150°, sulphur dioxide, water, and aromatic vapours being emitted. The corresponding acid, which forms shining, white needles, first acid and then intensely sweet to the taste, begins to decompose at 70—75°, with liberation of sulphur dioxide, m. p.

146° (decomp.). Treatment of the free acid in aqueous alcoholic solution with an alcoholic solution of the equivalent quantity of an aromatic base yields the salt of the base. *p*-Phenetidine *p*-phenetidino-methanesulphonate,

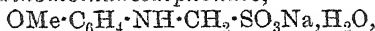


thus obtained, forms shining, white lamellæ, m. p. 137° (decomp.). When heated above the melting point, either sodium or *p*-phenetidine *p*-phenetidino-methanesulphonate yields a compound, $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_2\text{S}$, which forms lemon-yellow needles, m. p. 192—193°, and has the probable constitution

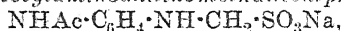


For derivatives of this class the name thioindamidines is suggested, the above compound being termed *p*-phenetidinothioindamidino-*p*-phenetidine.

Sodium p-anisidinomethanesulphonate,

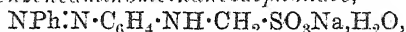


obtained from *p*-anisidine, formaldehyde, and sodium hydrogen sulphite, forms shining, white lamellæ; *sodium p-chloroanilino-methanesulphonate*, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{SO}_3\text{Na} \cdot \text{H}_2\text{O}$, shining, white scales with a greasy feel; *sodium p-toluidinomethanesulphonate* (compare Bucherer and Schwalbe, A., 1906, i, 828) crystallises with H_2O ; *sodium p-acetylaminomethanesulphonate*,



forms shining, white crystals, and the corresponding *acid*, crystals, m. p. 153—154° (decomp.).

Sodium azobenzeneaminomethanesulphonate,



obtained from aminoazobenzene, formaldehyde, and sodium hydrogen sulphite, forms shining, orange chips, and the corresponding *acid*, microscopic, purple crystals. This compound and the analogous one obtained from aminoazotoluene (m. p. 100°), behave normally towards potassium cyanide, giving the corresponding nitriles, from which the amides and thioamides may be prepared.

T. H. P.

Action of Alkalis and Acids on Sodium *p*-Phenetidino-methanesulphonate. II. ROBERTO LEPETIT (*Atti R. Accad. Lincei*, 1917, [v], 26, i, 172—174. Compare preceding abstract).

—The action of dilute sodium hydroxide solution on sodium *p*-phenetidino-methanesulphonate has been investigated with the object of obtaining anhydroformophenetidine, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{CH}_2$, but it is found that the action proceeds quantitatively according to the equation: $2\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{SO}_3\text{Na} + 2\text{NaOH} = (\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH})_2\text{CH}_2 + \text{CH}_2\text{O} + \text{H}_2\text{O} + 2\text{Na}_2\text{SO}_3$. Other arylamino-methanesulphonates undergo the same reaction, which represents a good general method for preparing imides. If pure methane-sulphonates are used, the di-imides are obtained in a pure state,

but on recrystallisation the melting point becomes lowered, owing to decomposition.

The action of boiling dilute hydrochloric acid on *p*-phenetidino-methanesulphonic acid yields *p*-phenetidine hydrochloride and a substance which crystallises in pale yellow, shining needles, and is the hydrochloride of a sulphur-free base, $C_{15}H_{20}O_2N_2$, m. p. 140° , exhibiting anæsthetic properties. When *p*-phenetidino-methanesulphonic acid is boiled with water alone, sulphur dioxide and formaldehyde are evolved, the residual product being the *p*-phenetidino-methanesulphonate of the above base.

$C_{15}H_{20}O_2N_2 \cdot OEt \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot SO_3H$, which crystallises in white needles, m. p. 160 — 161° , and exerts a pronounced and moderately persistent anæsthetic action.

T. H. P.

Preparation of Auromercaptobenzenes. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (U.S. Pat., 1207284, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 163).—Auromercaptobenzenes of the general formula $X \cdot S \cdot Au$ (where X is any benzene nucleus) are obtained by the action of double gold chlorides on mercaptobenzenes. They are yellow solids. The sodium salt of 4-amino-2-auromercaptobenzene-1-carboxylic acid is a yellow powder, readily soluble in water, insoluble in organic solvents.

H. W.

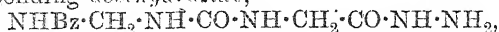
Mixed Chains containing Carbamide, Methylenediamine, and Amino-acid Residues. THEODOR CURTIUS (*J. pr. Chem.*, 1916, [ii], **94**, 85—134).—During his researches on acid azides, the author has obtained compounds which contain carbamide, methylenediamine, and glycine residues, for example, the substance of the formula

$NHPh \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot NH \cdot CO_2Et$ (A., 1904, i, 888). When such products are hydrolysed, they yield amino-acids, ammonia, amines, carbon dioxide, and formaldehyde, the above substance, for example, giving $NH_2Ph + 2CO_2 + 2NH_2 \cdot CH_2 \cdot CO_2H + 2NH_3 + H \cdot CHO + EtOH$. This is of considerable interest in view of the fact that the production of ammonia and carbon dioxide is also observed in the hydrolysis of proteins, and therefore the author has set out to synthesise complex compounds of the above type.

Two discoveries render this task fairly easy of accomplishment. The first is that carbimides are readily obtained by the decomposition of acid azides in indifferent media (Schroeter, A., 1909, i, 617; Stoermer, *ibid.*, 785; Curtius, A., 1913, i, 897), and the other that carbimides react easily with the esters of amino-acids (Fischer, A., 1906, i, 324) to form esters of carbamido-acids. If these are converted through the hydrazides and azides into the corresponding carbimides, condensation with further amino-acids is possible again, and so complex substances of the desired type can be built up. Some examples are now given.

[With ADRIEN LAURENT.]—I. *Combination of Hippenylcarbimide with Ethyl Glycine.*

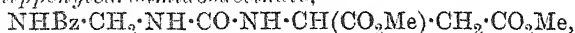
Hippuroylazide is converted into hippenylcarbimide (benzoyl-aminomethylcarbimide) (*ibid.*), and this is mixed with ethyl glycine, when *ethyl hippenylcarbamidoacetate* (benzoylaminomethylcarbamidoacetate) is formed, in white needles, m. p. 149—155°. The corresponding *acethydrazide*,



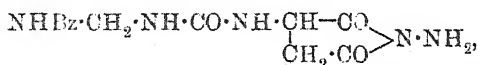
is obtained by boiling the ester with hydrazine hydrate, in microscopic needles, m. p. 206—207°. It yields benzoic acid, ammonia, formaldehyde, carbon dioxide, glycine, and hydrazine on hydrolysis, and these can be identified by suitable means. It also forms a *benzylidene* compound, m. p. 236°, but the corresponding azide has not been obtained pure.

[With WILLIAM F. ZIMMERLI.]—II. *Combination of Hippenylcarbimide and p-Bromohippenylcarbimide with Esters of l-Aspartic Acid.*

Methyl l-aspartate reacts with the above carbimide to form *methyl hippenylcarbamidossuccinate*,

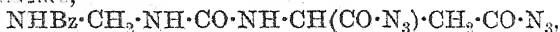


which crystallises in small granules, m. p. 153°. The corresponding *ethyl* ester forms small, white needles, m. p. 150°, and the free *acid* crystallises in rhombohedra, m. p. 159°, decomposes sodium carbonate, and gives an *ammonium* salt, m. p. 186° (decomp.), and a pale green *copper* salt. The *dihydrazide* forms microcrystalline granules, m. p. 102°, and yields a *dibenzylidene* compound, m. p. 212°, a *disalicylidene* compound, m. p. 206°, a *diisopropylidene* compound, m. p. 194°, and a *dibenzoyl* derivative, m. p. 207° (decomp.), when treated with the appropriate agents. The dihydrazide loses hydrazine when boiled with water, and changes into *N-aminohippenylcarbamidossuccinimide*,

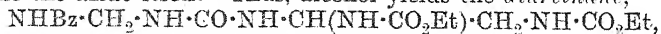


m. p. 144°, which also forms a *benzylidene* compound, m. p. 221°, which is acid to litmus.

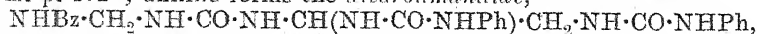
The dihydrazide is readily converted into *hippenylcarbamidossuccinyldiazide*,



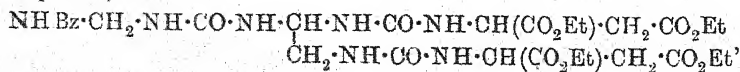
by the action of nitrous acid. This does not keep for more than a day or so, as it loses nitrogen easily, although without violence, and changes into the *dicarbimide*, m. p. 192°. For some of the reactions in which the carbimide is involved, it is therefore possible to use the azide itself. Thus, alcohol yields the *diurethane*,



m. p. 172°; aniline forms the *dicarbamanilide*,



m. p. 192°; *p*-toluidine gives an analogous compound, m. p. 195°. The dicarbimide also reacts with ethyl l-aspartate to form the compound,

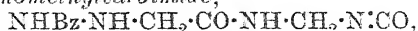


m. p. 124°. The corresponding tetrahydrazide and azide have been cursorily examined.

p-Bromohippenylcarbimide (*ibid.*) reacts with ethyl *l*-aspartate to form ethyl *p*-bromohippenylcarbamidossuccinate, slender needles, m. p. 162°, and this may be converted into the *dihydrazide*, m. p. 197°, and diazide in the usual way.

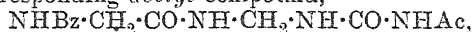
[With GEORG PETRIDIS.]—III. *Combination of Hippurylamino-methylcarbimide with Amides and Glycine Esters.*

Hippurylamino-methylcarbimide,



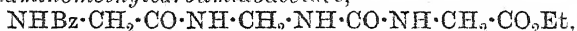
white leaflets, m. p. 122° (decomp.), is obtained from the corresponding azide (A., 1904, i, 833). New details are given in connexion with the preparation of this substance, including the statement that the necessary ethyl hippurylglycine can be obtained by benzoylating ethyl glycylglycine.

When boiled with water, this carbimide is transformed into *dihippurylamino-methylcarbimide* ["*diglycylhippenylcarbimide*"], $\text{CO}(\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NHBz})_2$, a white powder, m. p. 250° (decomp.), whilst alcohol converts it into ethyl hippurylamino-methylcarbamate, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, m. p. 202° (*ibid.*). It also reacts with benzamide to form *benzoylhippuryl-aminomethylcarbimide*, needles, m. p. 224°, and with acetamide to yield the corresponding *acetyl* compound,

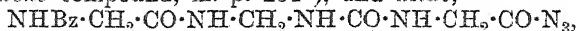


m. p. 179—180°.

The carbimide also reacts with ethyl glycine, yielding *ethyl hippurylamino-methylcarbamidoacetate*,

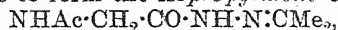


small, white needles, m. p. 179—180°. The corresponding free *acid* crystallises in slender needles, m. p. 204·5°, and forms an *ammonium* salt, m. p. 216°, and a *silver* salt, m. p. 191°, whilst the corresponding *amide*, m. p. 196°, *hydrazide*, silvery leaflets, m. p. 239° (*benzylidene* compound, m. p. 254°), and *azide*,



white needles, m. p. 113—114°, have also been obtained.

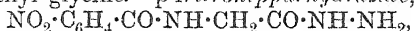
[*Supplementary.*]—I. With WILLIAM F. ZIMMERLI.—*Attempts to prepare Acetylaminooacetazide.*—Ethyl acetylaminooacetate is conveniently obtained by warming together ethyl glycine hydrochloride (1 mol.), anhydrous sodium acetate (a little more than 1 mol.), copper sulphate (about 0·1 mol.), and acetic anhydride (2 mols.), or by the action of acetyl chloride (compare Radenhausen, A., 1896, i, 137). The hydrazide is obtained from this by means of cold hydrazine hydrate (*ibid.*; *hydrochloride*, m. p. 177°). This reacts with acetone to form the *isopropylidene* compound,



m. p. 144°, but all attempts to convert it into the azide by means of nitrous acid resulted in the formation of diacetylglycylhydrazide, $\text{N}_2\text{H}_3(\text{CO}\cdot\text{CH}_2\cdot\text{NHAc})_2$, large leaflets, m. p. 259—260° (*ibid.*).

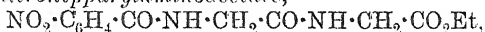
II. With GEORG PETRIDIS.—*Hydrazide and Azide of p-Nitrohippuric and p-Nitrohippurylaminoacetic Acids* (compare A., 1914, i, 871).—Ethyl *p*-nitrohippurate, m. p. 142° (Klages and Haack,

A., 1903, i, 560), and *ethyl o-nitrohippurate*, white needles, m. p. 81° , are readily obtained by the action of the nitrobenzoyl chlorides on ethyl glycine. *p-Nitrohippurhydrazide*,



forms slender, yellow needles, m. p. 203.5° , and yields a *benzylidene* compound, a yellow powder, m. p. 216° , and an *isopropylidene* compound, white leaflets, m. p. 211° . *p-Nitrohippurazide* is a fine, yellow powder, m. p. $70-72^{\circ}$ (decomp.), which decomposes within a few days.

Ethyl p-nitrohippurylaminoacetate,



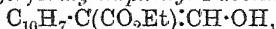
yellow needles, m. p. $172-173^{\circ}$, is obtained by acylating glycylglycine ester. The corresponding *hydrazide* crystallises in yellow leaflets, m. p. 249° , forms a *benzylidene* compound, m. p. 263° , and gives rise to the *azide*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{N}_3$, a voluminous, yellow powder, m. p. $91-92^{\circ}$ (decomp.).

III. With WILLIAM F. ZIMMERLI.—*Interaction of Hippenylcarbimide and Hydrochlorides of Amino-acid Esters*.—If, instead of using the free esters in the above reactions, hippenylcarbimide is treated with the hydrochlorides of methyl *L*-aspartate or ethyl glycine, the same abnormal compound, m. p. 215° , 13.1% N, is obtained.
J. C. W.

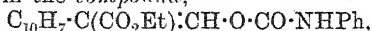
Ester Condensations with Naphthylacetic Esters. WILHELM WISLICENUS and HEINRICH ELVERT (*Ber.*, 1916, **49**, 2820—2830).—The esters of α - and β -naphthylacetic acids condense with ethyl formate under the influence of sodium to give formylnaphthylacetic esters. These exist in enol (" α ") and aldo (" β ") modifications.

For the preparation of the naphthylacetic esters, the methyl-naphthalenes are vigorously treated with bromine, the naphthylmethyl bromides are converted into nitriles, and warm alcoholic solutions of these are submitted to a brisk stream of hydrogen chloride. *Ethyl naphthyl-1-acetate* is a colourless oil, b. p. $177-179^{\circ}/13$ mm., and *ethyl naphthyl-2-acetate* has m. p. $31-32^{\circ}$, b. p. $186-187^{\circ}/14$ mm.

Enolic (" α ") *ethyl formylnaphthyl-1-acetate*,



crystallises from alcohol in glistening leaflets, m. p. $53-55^{\circ}$, gives a deep reddish-violet colour with ferric chloride, will keep for months in a desiccator or closed vessel, and combines with phenylcarbimide to form the compound,

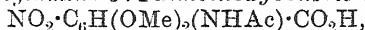


m. p. $79-80^{\circ}$. The β -modification crystallises from chloroform mixed with light petroleum in stellar aggregates of needles, m. p. $115-118^{\circ}$, does not react with phenylcarbimide, and is fairly stable at the ordinary temperature if contact with traces of alkali is avoided. Alcoholic solutions of the α -form quickly give a precipitate of the copper salt, $\text{Cu}(\text{C}_{15}\text{H}_{13}\text{O}_3)_2 \cdot \text{EtOH}$ (flat, green needles, m. p. $118-120^{\circ}$, or $192-194^{\circ}$ when free from alcohol), when treated with copper acetate; the β -modification reacts slowly, apparently

after isomerisation. Solutions of the potassium salt give precipitates of the β -modification when added to sulphuric acid, copper sulphate, or ferric chloride solutions, but if treated with a current of carbon dioxide, or if these salts are added to the solution, then the free ester or the copper or ferric salts of the α -form are obtained.

The α -form of *ethyl formyl-naphthyl-2-acetate*, m. p. 50—51°, is best obtained by converting the crude mixture of the two modifications into the *copper* salt, m. p. 186—188°, and decomposing this by dilute sulphuric acid. It gives a deep bluish-violet colour with ferric chloride. The β -modification, m. p. 86—87°, is formed when the solution of the potassium salt is stirred into 30% sulphuric acid. It changes more readily into the α -form than the corresponding ester of formyl-naphthyl-1-acetic acid. J. C. W.

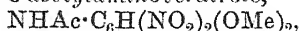
The Nitration of 2-Acetyl-amino-3:4-dimethoxybenzoic Acid and 3-Acetylaminoveratrole. CHARLES STANLEY GIBSON, JOHN LIONEL SIMONSEN, and MADYAR GOPALA RAU (T., 1917, 111, 69—85).—On nitration of 2-acetyl-amino-3:4-dimethoxybenzoic acid, 6-nitro-2-acetyl-amino-3:4-dimethoxybenzoic acid,



was obtained as sole product; this substance, when cautiously hydrolysed with sulphuric acid, gave 6-nitro-2-amino-3:4-dimethoxybenzoic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}(\text{OMe})_2(\text{NH}_2) \cdot \text{CO}_2\text{H}$, but when heated with somewhat diluted hydrochloric acid was converted into 5-nitro-3-aminoveratrole, $\text{NO}_2 \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{NH}_2$, with loss of carbon dioxide. 5-Nitro-3-aminoveratrole was also obtainable in the form of its acetyl derivative by the nitration of 3-acetylaminoveratrole (see below).

By means of the diazo-reaction, 5-nitro-3-aminoveratrole was converted through the *nitrile*, $\text{NO}_2 \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{CN}$, into 5-nitro-2:3-dimethoxybenzoic acid, which has already been described (Cain and Simonsen, T., 1914, 105, 159). 6-Nitro-2:3-dimethoxybenzoic acid, whatever its method of preparation, has m. p. 185—186° (Perkin and Robinson, T., 1914, 105, 2390, gave 178·5°; compare also Wegscheider and Klemenc, A., 1910, i, 670).

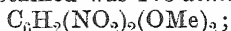
In the nitration of 2-acetyl-amino-3:4-dimethoxybenzoic acid, especially under slightly modified conditions, there was also obtained 4:5-dinitro-3-acetylaminoveratrole,



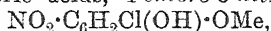
which is soluble in aqueous alkalis; this was also produced, together with 5:6-dinitro-3-acetylaminoveratrole, by the nitration of 3-acetylaminoveratrole or of 5-nitro-3-acetylaminoveratrole, which were prepared from 3-aminoveratrole by acetylation or successive acetylation and nitration respectively. When heated with sulphuric acid, the 4:5-dinitro-3-acetylaminoveratrole was converted into 4:5-dinitro-3-aminoveratrole, $\text{NH}_2 \cdot \text{C}_6\text{H}(\text{NO}_2)_2(\text{OMe})_2$; in a similar manner, the 5:6-dinitro-3-acetyl-amino-isomeride yielded 5:6-dinitro-3-aminoveratrole.

When 4:5-dinitro-3-aminoveratrole was diazotised in alcoholic

solution, the product obtained was 4:5-dinitroveratrole,



but on diazotisation in acetic acid containing a little sulphuric acid, scission of a methyl group occurred, the product of coupling with β -naphthol being 4:5-dinitro-2-hydroxy-1-methoxy-3-azo- β -naphthol, $\text{OH}\cdot\text{C}_6\text{H}(\text{OMe})(\text{NO}_2)_2\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$; somewhat similarly, on heating the solution obtained by diazotising in a mixture of acetic and hydrochloric acids, 4-chloro-5-nitroguaiacol,



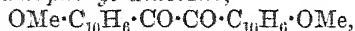
was formed. By diazotisation in alcoholic solution, 5:6-dinitro-3-aminoveratrole was converted into 3:4-dinitroveratrole, which was accompanied by a small quantity of a phenolic substance.

[With J. E. PURVIS.]—On account of the solubility of 4:5-dinitro-3-acetylaminoveratrole in alkali to a yellow solution, whereas the 5:6-dinitro-isomeride is insoluble, the absorption spectra of these substances have been examined, the results indicating that the solubility in the former case is not due to any marked constitutional change.

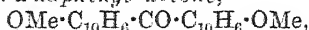
For details, the original paper should be consulted. D. F. T.

Preparation of Seleno-phthaleins and their Halogen Derivatives. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 295253, addition to D.R.-P., 290540, 291883; from *J. Soc. Chem. Ind.*, 1917, 36, 211).—In place of the phthalins specified in the previous patents (A., 1916, i, 560, 728), their *O*-acetyl compounds or *O*-acetyl compounds of phthaleins are used in indifferent solvents. The products are different from those obtained by the action of selenium on fluoresceins in aqueous alkaline solution in accordance with D.R.-P., 279549 (compare A., 1915, i, 409). H. W.

Action of Oxalyl Chloride on Ethers of the Naphthols. M. GIUA (*Gazzetta*, 1917, 47, i, 51—57).—The action of oxalyl chloride on α -naphthyl methyl ether in light petroleum solution and in presence of aluminium chloride yields: (1) mainly 4:4'-dimethoxydi- α -naphthyl diketone,

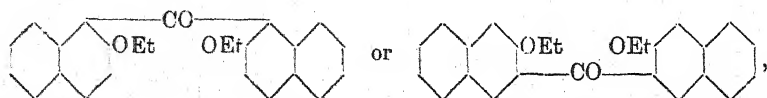


which forms pale yellow needles, m. p. 230—231°, and gives a red coloration with concentrated sulphuric acid; (2) a small proportion of 4:4'-dimethoxydi- α -naphthyl ketone,



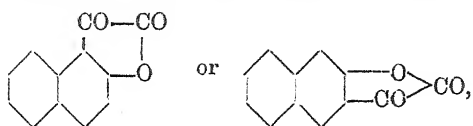
which forms shining, white plates, m. p. 142°, and gives a yellowish-red coloration with concentrated sulphuric acid.

The same reaction with β -naphthyl ethyl ether in carbon disulphide yields: (1) the diethoxydinaphthyl ketone,



which forms small, white prisms, m. p. 184°, and gives a pale yellow

coloration with concentrated sulphuric acid; (2) the lactone of



a hydroxynaphthylglyoxylic acid (annexed formulæ), which crystallises in orange-yellow needles, m. p. 178° (decomp.), and gives a

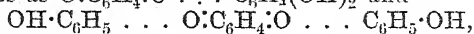
carminic coloration with concentrated sulphuric acid. T. H. P.

Coloured Organic Molecular Compounds. PAUL PFEIFFER [with W. JOWLEFF, PH. FISCHER, P. MONTI, and H. MULLY] (*Annalen*, 1916, **412**, 253—335. Compare A., 1914, i, 551).—It has already been indicated (*loc. cit.*) that the most important groups of coloured organic molecular compounds are probably closely related in type with the halochromic compounds of the aldehydes, ketones, and acids. By analogy, therefore, it would be expected that nitro-compounds should be capable of forming halochromic compounds with metallic salts and acids in the same manner as do ketones, and such compounds have now been observed with unsaturated nitro-compounds, such as the nitrostilbenes and nitrostyrenes. The colour of all these molecular compounds is referred to the one-sided saturation effected at the double linking of the group by which attachment is made; thus, in the ketones and nitro-compounds, the uneven distribution of the saturation must leave a certain amount of free valency at the carbon and nitrogen atoms respectively, as may be represented by the formulæ $R_2C:O \dots A$ and

$RNO_2 \dots A$, where the arrow represents the free valency and A the

molecule of the second constituent; on account of the degree of unsaturation thus produced in it, the carbon or nitrogen atom assumes the character of a chromophore. In some of the types of molecular compounds, such as the quinhydrones, the second molecule probably contributes considerably to the colour of the compound by supplying a second chromophoric atom, thus, $R_2C:O \dots C:C$.

The formulation of the coloured additive compounds of phenols with quinones as $O:C_6H_4:O \dots C_6H_4(OH)_2$ and



is confirmed by the fact that quinones can form with aromatic hydrocarbons coloured additive compounds resembling the quinhydrones in stability; the hydroxyl or amino-radicle is therefore not essential to the formation of "quinhydrone" compounds, neither, indeed, is hydrogen itself, because hexamethylbenzene is capable of yielding coloured additive compounds with quinones. It is therefore necessary to assume that the power of forming quinhydrone compounds with quinones is due to the benzene nucleus of the second reagent, and the fact that hexahydrodurene does not produce any colour reaction with quinones, whilst durene itself does, is in agreement with this assumption. Terpenes and un-

saturated compounds, such as dimethylbutadiene, dissolve quinones, giving more or less deeply coloured solutions, and this effect is doubtless to be attributed to the unsaturated condition, in which these hydrocarbons resemble the benzene hydrocarbons.

Not only *p*-quinones, but also *o*-quinones, such as phenanthraquinone, are able to form additive compounds with benzene hydrocarbons, for example, hexamethylbenzene. It is found that with the quinhydrones, methyl groups present in the quinonoid constituent have a hypsochromic effect on the colour, whilst methyl groups in the benzenoid component exert a bathochromic influence; the effect of methoxyl and hydroxyl groups is similar to that of the methyl group, but halogen atoms, on the contrary, exert a bathochromic effect when in the quinonoid nucleus and a hypsochromic effect in the benzenoid component.

The constitution of the compounds of hydrocarbons with nitro-compounds is likewise explained as due to attachment between the unsaturated nitro-group and the unsaturated hydrocarbon nucleus (compare Werner, A., 1910, i, 20). Accordingly, the analogy between compounds of the type $R \cdot NO_2 \dots C_6H_6$ and of the type $R_2CO \dots C_6H_6$ is a close one. *s*-Trinitrobenzene is especially well adapted to the formation of additive compounds with aromatic hydrocarbons, and in view of this result, the compounds of these hydrocarbons with picric acid are not to be regarded as "picrates," but should be represented by $OH \cdot C_6H_2(NO_2)_3 \dots C_nH_m$, that is, as the hydroxyl derivatives of the corresponding trinitrobenzene compounds. Once more it is found that the methyl groups in the benzenoid component are bathochromic in influence, but are hypsochromic in the nitro-constituent. By analogy with the hydrocarbon derivatives, and because of the regularity of the effects produced on introducing the various substituents, the additive compounds of the nitro-compounds with phenols and amines must be represented $R \cdot NO_2 \dots C_6H_5 \cdot OH$ and $R \cdot NO_2 \dots C_6H_5 \cdot NH_2$.

The analogy between nitro-compounds and ketones in the formation of molecular compounds leads to the expectation of additive compounds between nitro-compounds and metallic salts or acids; nitro-compounds containing ethylenic linkings exhibit more pronounced halochromic phenomena than do ordinary aromatic nitro-compounds, and their methyl or methoxy-derivatives are especially noteworthy in this respect. Only in relatively few cases have the solid halochromic compounds been isolated, the formation being in most cases assumed from the colour of the solution of the substance, for example, in acetic acid or trichloroacetic acid.

The stannic chloride additive compounds of the ketones are represented as of the structure $SnCl_4 \begin{smallmatrix} \text{O} \cdot \text{CRR}' \\ \text{O} \cdot \text{CRR}' \end{smallmatrix}$, and the perchloric acid derivatives (compare Hofmann and others, A., 1910, i, 105, 168, 187, 370, 818), which also possess equimolecular constitution, are also regarded as containing the acid molecule linked to the ketone molecule, only through the oxygen atom, thus,

$$RR'/C \cdot O \dots HClO_4$$

With other acids, there is a tendency for the ketone to bind more

than a molecular proportion of acid, and it is believed that in these cases the constitution is still the same and that the acid has reacted in a polymerised condition. For the purpose of examining the halochromy with these compounds, the stannic chloride compounds are compared in the crystalline condition, whilst the perchlorates, on account of their tendency to exhibit surface lustre, are compared in solution. The interposition of ethylene linkings between the benzene nucleus and the carbonyl group deepens the colour of the additive compounds. A colour comparison of the stannic chloride and sulphuric acid additive compounds of hydroxybenzophenone and hydroxyxanthone with the alkaline solutions of these substances reveals a notable similarity, suggesting that the colour of the alkali salts is due to halochromy, and that the constitution of these salts

should be represented $C_6H_4 \begin{matrix} \diagup O-M \\ \diagdown CR:O \end{matrix}$, where M is the metallic atom.

The following *additive* compounds are described: *chloro-p-benzoquinone-hexamethylbenzene*, $C_6H_3O_2Cl, C_6Me_6$, orange-coloured needles, m. p. 99—103°; *2:5-dichloro-p-benzoquinone-durene*, $C_6H_3O_2Cl_2, 2C_6H_2Me_4$, orange-yellow tablets, m. p. 82—86°; *2:5-dichloro-p-benzoquinone-hexamethylbenzene*,

$C_6H_2O_2Cl_2, C_6Me_6$, red needles, m. p. 132—136°; *tetrachloro-p-benzoquinone-hexamethylbenzene*, $C_6O_2Cl_4, C_6Me_6$, violet-brown needles, m. p. 198—202°; *tetrabromo-p-benzoquinone-hexamethylbenzene*,

$C_6O_2Br_4, C_6Me_6$, deep violet-brown needles, m. p. 198—203°; *tetrachloro-o-benzoquinone-benzene*, $C_6O_2Cl_4, 3C_6H_6$, deep red crystals, m. p. 37—42°; *tetrachloro-o-benzoquinone-toluene*, $C_6O_2Cl_4, C_6H_5Me$, deep red needles, m. p. 45—50°; *tetrachloro-o-benzoquinone-p-xylene*,

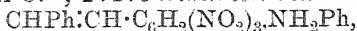
$C_6O_2Cl_4, C_6H_4Me_2$, deep red prisms, m. p. near 83°; *tetrachloro-o-benzoquinone-hexamethylbenzene*, $C_6O_2Cl_4, C_6Me_6$, greenish-black needles, m. p. 140—143°; *phenanthraquinone-hexamethylbenzene*,

$C_{14}H_8O_2, C_6Me_6$, orange needles, m. p. 160—163°.

s-Trinitrobenzene-toluene, $C_6H_3(NO_2)_3, C_6H_5Me$, very pale yellow needles; *s-trinitrobenzene-xylene*, $C_6H_3(NO_2)_3, C_6H_4Me_2$, greenish-yellow needles; *s-trinitrobenzene-durene*, $C_6H_3(NO_2)_3, C_6H_2Me_4$, greenish-yellow leaflets, m. p. 92—98; *s-trinitrobenzene-hexamethylbenzene*, yellow needles, m. p. 174—175°; *s-trinitrobenzene-stilbene*, $2C_6H_3(NO_2)_3, C_2H_2Ph_2$, golden-yellow needles, m. p. indistinct at 107—110°; *s-trinitrobenzene-hexamethylstilbene*, cinnabar-red prisms, m. p. 145—147°; *s-trinitrobenzene-pp'-dimethoxystilbene*, $2C_6H_3(NO_2)_3, C_2H_2(C_6H_4 \cdot OMe)_2$, red needles, m. p. 145—155° (decomp.); *2:4-dinitrodeoxybenzoin-aniline*,

$COPh \cdot CH_2 \cdot C_6H_3(NO_2)_2, NH_2Ph$, golden-yellow leaflets, m. p. near 91°; *2:4-dinitro-4'-methyldeoxybenzoin-aniline*, $C_6H_4Me \cdot CO \cdot CH_2 \cdot C_6H_3(NO_2)_2, NH_2Ph$, yellow, leafy needles, m. p. 68°; *2:4-dinitro-4'-methoxydeoxybenzoin-aniline*, $OMe \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot C_6H_3(NO_2)_2, NH_2Ph$, yellow, leafy

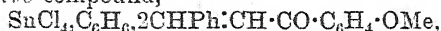
needles, m. p. near 87° ; 2:4:6-trinitrostilbene—*aniline*,



orange-red leaflets, m. p. $103\text{--}105^{\circ}$; 2:4:6-trinitrostilbene—*dimethylaniline*, $\text{CHPh}\cdot\text{CH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{NPhMe}_2$, violet-brown leaflets, m. p. near 120° ; 2:4:6-trinitrostilbene—*o-toluidine*, $\text{CHPh}\cdot\text{CH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, red leaflets, m. p. near 120° . Many of the above compounds gradually decompose in the atmosphere, losing their volatile constituent.

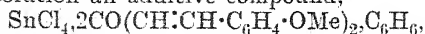
The dinitrodeoxybenzoin (compare Borsche, A., 1912, i, 652) used above was also converted into its *oxime*, yellow needles, m. p. $137\text{--}139^{\circ}$; the 2:4-dinitrophenylacetyl chloride used in its preparation gave a corresponding *anilide*, $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, yellow needles, m. p. $181\text{--}182^{\circ}$, and a *phenylhydrazide*, yellow needles, m. p. $174\text{--}176^{\circ}$. 2:4-Dinitro-4'-methyldeoxybenzoin, brownish-yellow needles, m. p. $135\text{--}136^{\circ}$, or less stable yellow leaflets, m. p. $95\text{--}96^{\circ}$, was prepared by the Friedel-Crafts' reaction with 2:4-dinitrophenylacetyl chloride and toluene in carbon disulphide, whilst 2:4-dinitro-4'-methoxydeoxybenzoin, yellow needles, m. p. $101\text{--}103^{\circ}$, was obtained in a similar manner, using anisole in place of toluene.

p-Anisyl styryl ketone in benzene solution with stannic chloride gave an *additive* compound,

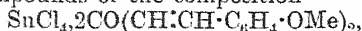


yellow crystals, m. p. near 105° . Phenyl *o*-methoxystyryl ketone, very pale yellow needles, m. p. $64\text{--}65^{\circ}$, prepared by the methylation of the corresponding hydroxyl compound, yielded an *additive* compound, $\text{SnCl}_4\cdot 2\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COPh}$, a red, crystalline powder, m. p. near $135\text{--}136^{\circ}$; in the preparation of the parent ketone by the condensation of anisaldehyde and acetophenone, *o*-anisylidenediacetophenone, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{CH}_2\cdot\text{COPh})_2$, colourless needles, m. p. $113\text{--}114^{\circ}$, was also obtained.

Phenyl *m*-methoxystyryl ketone, pale yellow leaflets, m. p. 64° , obtained by the methylation of the corresponding hydroxy-compound and also by the direct condensation of *m*-methoxybenzaldehyde with acetophenone, formed the *additive* compound, $\text{SnCl}_4\cdot 2\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COPh}$, compact, yellow crystals, m. p. $100\text{--}110^{\circ}$. Phenyl *p*-methoxystyryl ketone gave an orange-red, crystalline *additive* compound of the same composition, m. p. $105\text{--}110^{\circ}$. Styryl *p*-methoxystyryl ketone gave an *additive* compound, $\text{SnCl}_4\cdot\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, a red, crystalline powder, m. p. near 172° . Di-*o*-methoxydistyryl ketone yielded from benzene solution an *additive* compound,

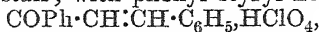


orange-red crystals, m. p. 180° ; the *meta* and *para* isomerides both gave *additive* compounds of the composition

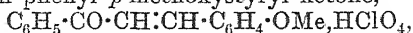


orange-yellow crystals, m. p. near 170° , and a crystalline, black powder respectively. Dimethylenedioxydistyryl ketone yielded the compound, $\text{SnCl}_4\cdot 2\text{CO}(\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_3\cdot\text{O}_2\cdot\text{CH}_2)_2$, as a black precipitate from benzene solution. Styryl cinnamylidenemethyl ketone gave the compound, $\text{SnCl}_4\cdot 2\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHPh}$, copper-red leaflets, m. p. near 171° .

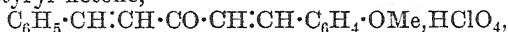
The following *additive* compounds with perchloric acid were prepared: with *p*-methoxybenzophenone, $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}, \text{HClO}_4$, yellowish-brown crystals; with phenyl styryl ketone,



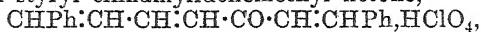
yellow crystals, decomp. at $92-96^\circ$; with *p*-anisyl styryl ketone, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh}, \text{HClO}_4$, orange-yellow crystals, m. p. $63-78^\circ$; with phenyl *p*-methoxystyryl ketone,



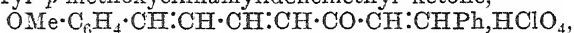
orange-red crystals with a blue glance, m. p. $103-107^\circ$; with styryl *p*-methoxystyryl ketone,



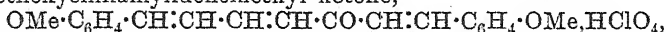
violet needles with a blue glance, m. p. $123-125^\circ$; with *pp'*-dimethoxydistyryl ketone, $\text{CO}(\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2, \text{HClO}_4$, violet-black crystals with green glance, decomp. at $160-162^\circ$; *oo'*-dimethoxydistyryl ketone, violet, crystalline powder with green glance; with styryl cinnamylidenemethyl ketone,



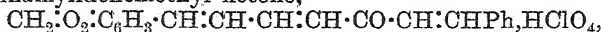
red needles with a faint green lustre, m. p. $156-163^\circ$ (decomp.); with styryl *p*-methoxycinnamylidenemethyl ketone,



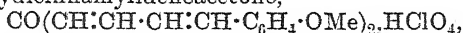
steel-blue needles with a feeble green lustre, m. p. $133-147^\circ$ (decomp.); with styryl *m*-methoxycinnamylidenemethyl ketone, a product of the same composition, violet-black crystals with green lustre, m. p. $155-157^\circ$ (decomp.); with *p*-methoxystyryl *p*-methoxycinnamylidenemethyl ketone,



deep bluish-violet needles with green glance; with styryl methylene-dioxy-cinnamylidenemethyl ketone,



blackish-violet needles with green glance, m. p. $138-151^\circ$; with dicinnamylideneacetone, $\text{CO}(\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHPh})_2, \text{HClO}_4$, bluish-violet needles with blue glance, decomp. $130-148^\circ$; with *pp'*-dimethoxydicinnamylideneacetone,



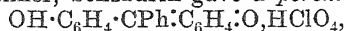
indigo-blue needles with green lustre, decomp. near 150° .

For the production of the last-named additive compounds, the preparation of the following ketones was necessary: *styryl p*-methoxycinnamylidenemethyl ketone, yellow crystals, m. p. $115-116^\circ$; *styryl m*-methoxycinnamylidenemethyl ketone, yellow needles, m. p. $99-101^\circ$; *p*-methoxystyryl *p*-methoxycinnamylidenemethyl ketone, yellow needles, m. p. $146-148^\circ$; *pp'*-dimethoxydicinnamylideneacetone, greyish-yellow leaflets, m. p. $167-168^\circ$, the turbid fusion becoming clear at $177-180^\circ$; *p*-methoxycinnamylidenemethyl methyl ketone, yellow leaflets, m. p. $107-108.5^\circ$. The general method of synthesis was the condensation of the required aldehyde and ketone in the presence of alkali; thus, styryl *m*-methoxycinnamylidenemethyl ketone was obtained by the interaction of styryl methyl ketone and *m*-methoxycinnamaldehyde (*phenylhydrazone*, m. p. $105-106^\circ$).

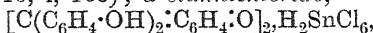
Fuchson yielded a *perchlorate*, $\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}, \text{HClO}_4$, red needles with blue glance, m. p. near $215-216^\circ$; a *stannichloride*, $(\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{O})_2\cdot\text{H}_2\text{SnCl}_6$, red needles with blue glance, m. p.

210—211°; and a *stannibromide*, $(\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{O})_2\cdot\text{H}_2\text{SnBr}_6$, red prisms with green glance, m. p. 204—205°.

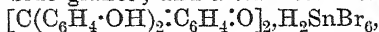
In a similar manner, benzaurin gave a *perchlorate*,



orange-coloured needles with green lustre; a *stannichloride*, $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{O})_2\cdot\text{H}_2\text{SnCl}_6$, orange-coloured crystals with green lustre, m. p. 268—269° (decomp.); and a *stannibromide*, $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{O})_2\cdot\text{H}_2\text{SnBr}_6$, compact, red crystals with green lustre, m. p. 256—257° (decomp.). Aurin formed a perchlorate, $\text{C}(\text{C}_6\text{H}_4\cdot\text{OH})_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{HClO}_4$ (compare Hofmann, Kirmreuther, and Thal, A., 1910, i, 168); a *stannichloride*,

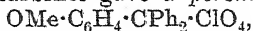


red crystals with blue glance; and a *stannibromide*,



red crystals with blue glance.

p-Methoxytriphenylcarbinol gave a *perchlorate*,



orange crystals, but no stannichloride was obtainable. D. F. T.

Ozone and its Action on Organic Compounds. CARL DIETRICH HARRIES (*Chem. Zentr.*, 1916, ii, 991—995).—The author has published in book form (1916, pp. 712) an account of his investigations on the action of ozone on organic compounds; the greater part of the results has been previously described, but the following investigations have not heretofore been communicated.

[With KURT OPPENHEIM].—*Identification of Aliphatic Aldehydes*.—The general reactions for aldehydes have been examined for a series of aliphatic aldehydes. It has been found that the semicarbazones of the lower aldehydes can only be induced to crystallise with great difficulty, whereas the higher aldehydes immediately yield crystalline products. Conversely, the nitrophenylhydrazones of the higher aldehydes are oily, those of the lower members being crystalline. All the aldehydes investigated gave good results with diphenylmethanedimethyldihydrazine (Braun, A., 1908, i, 700). Unsatisfactory results were obtained in attempting to apply Angeli's reaction (action of benzenesulphohydroxamic acid and conversion of the hydroxamic acids formed into their copper salts) to the exact characterisation of aldehydes.

Propaldehyde has D_{16}^{19} 0.8171; n_D^{19} 1.36460; n_a 1.36284; n_γ 1.37315; M_D 15.84; $M_{\gamma-a}$ 0.4. The aldehyde-ammonia compound decomposes at 0°; semicarbazone, oily; *nitrophenylhydrazone*, yellow needles, m. p. 124°. Braun's reagent gives a crystalline compound, $\text{C}_2\text{H}_5\text{H}_{28}\text{N}_4$, m. p. 45°. With pyruvic acid and naphthylamine (Döbner, A., 1894, i, 261, 532) the corresponding *naphthacinchonic acid*, m. p. 278—281°, is formed. The copper salt, prepared in accordance with Angeli's method, gives too high values for copper.

n-Butaldehyde, isolated from the bisulphite compound, has D_{20}^{20} 0.8048; n_D^{20} 1.38356; n_a 1.38113; n_γ 1.39137; M_D 20.9; mol. dispersion 0.49. It yields a crystalline *semicarbazone* (after a

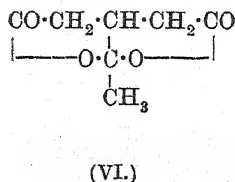
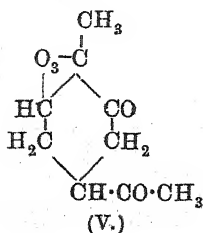
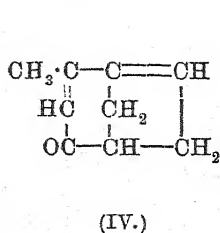
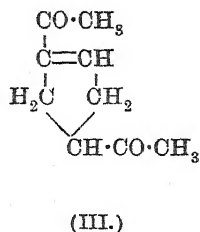
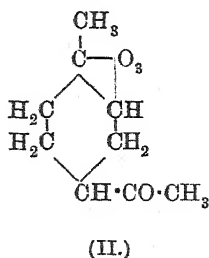
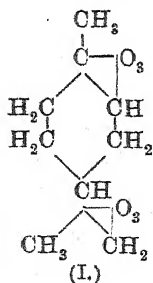
long time), m. p. about 77° . The *nitrophenylhydrazone* forms yellow needles, m. p. 87° . Braun's reagent gives a compound, m. p. 70.5° . The *naphthacinchonic acid* from butaldehyde crystallises in needles, m. p. 248° . Angeli's reaction gives a green, copper salt. *iso*Butaldehyde has D_{20}^{25} 0.7917, n_D^{25} 1.37326; n_a 1.37117; n_{γ} 1.38271; M_D 20.71; mol. dispersion, 0.58. The *semicarbazone* crystallises in prisms, m. p. 121° ; the *nitrophenylhydrazone* forms yellow crystals, m. p. 130° . Braun's reagent gives the compound, $C_{23}H_{32}N_4$, yellow crystals. With Döbner's reagent the substance, $C_{17}H_{15}O_2N$, needles decomposing at about 260° , is formed. Angeli's reaction gives results similar to those obtained with the normal aldehyde. *iso*Valeraldehyde (from the bisulphite compound) has b. p. 92° ; D_{20}^{25} 0.7845; n_D^{25} 1.39023; n_a 1.38789; n_{γ} 1.39940; M_D 25.9; mol. dispersion, 0.7. The *thiosemicarbazone* and *nitrophenylhydrazone*, yellow plates, have m. p.'s $52-53^{\circ}$ and 101° respectively. Braun's reagent yields the substance, $C_{25}H_{36}N_4$, yellow prisms, m. p. 85° . The compound, $C_{18}H_{17}O_2N$, m. p. 250° , is formed by Döbner's reaction. *n*-Heptaldehyde has b. p. 154° , D_{20}^{25} 0.8320; n_D^{25} 1.41370; n_a 1.41105; n_{γ} 1.42312; M_D 34.59; mol. dispersion, 0.88. The crystalline *semicarbazone* has m. p. 109° ; *nitrophenylhydrazine* and *bromophenylhydrazine* yield oily precipitates. Reduction of heptaldehyde by sodium amalgam in acetic acid solution yields *n*-heptyl alcohol, b. p. $90^{\circ}/14$ mm. If, however, an excess of sodium is avoided and the solution is not kept acid, diheptylenealdehyde, $CH_3 \cdot [CH_2]_5 \cdot CH : C(CHO) \cdot [CH_2]_4 \cdot CH_3$, D_{20}^{25} 0.8463, is produced (compare Perkin, T., 1883, 43, 67). Octaldehyde has b. p. $171-173^{\circ}$; D_{20}^{25} 0.82583; n_D^{25} 1.42167; n_a 1.41957; n_{γ} 1.43175; M_D 39.3; mol. dispersion, 1.00. The *semicarbazone* has m. p. 98° , whilst the *nitrophenylhydrazone* and *bromophenylhydrazone* are oily. Braun's reagent gives the substance $C_{31}H_{48}N_4$, yellow plates, m. p. 60° . The *naphthacinchonic acid* of octaldehyde, $C_{21}H_{23}O_2N$, forms yellow leaflets, m. p. $240-243^{\circ}$. The copper salt prepared by Angeli's method gives low analytical values for copper. Nonaldehyde has D_{20}^{25} 0.8268; n_D^{25} 1.42417; n_a 1.41876; n_{γ} 1.43357; M_D 43.8; mol. dispersion, 1.323. It yields an oily precipitate with *nitrophenylhydrazine*, whilst Braun's reagent gives the substance, $C_{33}H_{55}N_4$, yellow leaflets, m. p. 61° . Attempts to separate mixtures of aldehydes by fractional distillation or by conversion into derivatives were unsuccessful.

[With HEINRICH NERESHEIMER.]—*Action of Ozone on certain Terpenes.*—The action of ozone on *d*-limonene in carbon tetrachloride solution leads to the formation of a solid *ozonide*, which when dissolved in ethyl acetate leaves a small residue, probably consisting of oxozonide; the latter passes after some time into the ozonide (formula I). This substance forms a white mass, m. p. $60-65^{\circ}$, $[\alpha]_D^{18} -9.32^{\circ}$, in chloroform solution, which decomposes violently at about 85° . Short treatment with boiling water or dilute acetic acid transforms the ozonide into the *keto-ozonide* (formula II), $C_9H_{14}O_4$, which is a syrup; protracted treatment with boiling water leads to the formation of the diketaldehyde, $CH_3 \cdot CO \cdot [CH_2]_2 \cdot CH(CO \cdot CH_3) \cdot CH_2 \cdot CHO$, from which the sub-

stances (formulae III and IV) are formed by ring closure, and cannot be separated from one another. Total decomposition of the diozonide by treatment with boiling water during twenty-four hours results in the formation of an oil, b. p. 130—140°/9 mm., from which definite derivatives were not obtained. Oxidation of the ozonide by chromic acid in acetic acid solution at 50—60° leads to the formation of $\beta\delta$ -diacetylvaleric acid. In addition to the fairly stable normal ozonides, the ketones yield highly explosive ozonide peroxides. Decomposition with water causes the formation of the acids expected according to theory. 1-Methylcyclohexene-3-one, when ozonised in chloroform or acetic acid solution, gives a greenish-yellow, very explosive oil, readily soluble in all media except light petroleum. The substance, which is probably the ozonide peroxide, gives the hydrogen peroxide reaction and reduces Fehling's solution after short treatment with boiling water. γ -Acetylbutyric acid (m. p. of hydrate, 38°) is obtained when its aqueous solution is evaporated to dryness in a vacuum.

A mixture of normal *ozonide* and *ozonide peroxide*, a yellow, explosive liquid, is formed by ozonising pulegone in chloroform solution, which is converted by water into β -methyladipic acid. The latter substance, $\alpha_D + 2.5^\circ$ (in 33% aqueous solution, $l=1$), is also obtained by evaporation of the chloroform solution of the mixture.

A solution of carvone in carbon tetrachloride is converted by ozone into the oily *carvonediozonide*, which, when further ozonised in the same solvent, yields *carvonediozonide peroxide*, unstable, yellow syrup, which explodes after a few hours in a freezing mixture, more rapidly on contact with ice-water and within thirty to thirty-five seconds after mixture with water at 40°. Formaldehyde is formed during the explosion, together with an oil, $C_9H_{12}O_5$, which in all probability is the diketo-ozonide (formula V). Total



decomposition of the diozonide by steam yields β -acetylglutaric acid (or its ketodilactone, VI), which is also formed from the diketo-ozonide and boiling water.

[With HANS VON SPLAWA-NEYMAN.]—*An Aldehyde from Pinene* (Addendum to A., 1909, i, 247).—Pinonaldehyde, $C_{10}H_{16}O_2$, is a pale yellow oil, b. p. 115–125°, D_4^{19} 1.022, n_D^{19} 1.46867; n_D^{20} 1.46531; M_D 45.75; $[\alpha]_D^{20} + 14.67^\circ$. It is readily volatile with steam, reduces cold silver and Fehling's solutions, and is oxidised by air with formation of pinonic acid. It is readily changed by acids and alkalis or by gentle heating. It reacts with nitrophenylhydrazine. When warmed with benzenesulphohydroxamic acid and acidified, it gives a red coloration with ferric chloride and with copper acetate a green precipitate of the *copper* salt of the corresponding hydroxamic acid. Pinonic acid, obtained by oxidation of the aldehyde with aqueous potassium permanganate, is an oil, b. p. 180–188°/12 mm., $[\alpha]_D^{20} + 3.9^\circ$ in chloroform solution. The crystalline *semicarbazone*, $C_{11}H_{16}O_3N_3$, has m. p. 204°. Nopinone, pleasant-smelling oil, $[\alpha]_D^{19} + 45^\circ$ (*semicarbazone*, m. p. 167°; *benzylidene* derivative, m. p. 106–107°), is obtained by oxidising the previously described (*loc. cit.*) oil (obtained by fusion of pineneozonide) with permanganate.

[With ROBERT VINER STANFORD.]—*Degradation of Sericin by Ozone* (compare Harries and Langheld, A., 1907, i, 571).—When sericin is ozonised in aqueous solution the products of fission only account for 65% of the original material. The sole uniform product which is formed is a *polypeptide*, which, after purification by repeated solution in water and precipitation with methyl alcohol, has $[\alpha]_D^{18.5} - 60.1^\circ$, C=43.9%, H=5.85%, N=17.5%. Determinations of molecular weight lead to the formula $C_{29}H_{43}O_{16}N_{10}$. It yields a brown *silver* salt, a *lead* compound with lead acetate and ammonia, and a microcrystalline *hydriodide*, containing 14.37% of iodine. Hydrolysis of the polypeptide by acids yielded: CO_2 , 8.8%; NH_4Cl , 9.2%; glycine, about 0.5%; alanine, about 1%; valine (or leucine), about 0.3%; serine, 13.1%; aspartic acid, 0.25%; glutamic acid, 0.25%; lysine, 0.35%; and, in addition, arginine. The phenyl group contained in sericine cannot be recognised among the products of ozonisation.

[With EDGAR PAULSEN.]—*Resins*.—A fundamental difference exists between the ozonides of caoutchouc and dammar resin, since the latter is insoluble in carbon tetrachloride and not explosive. Decomposition with water leads to the formation of only a small quantity of acid, the main substance being a solid fission product, insoluble in water. Since other resins behave similarly to dammar resin, it is possible to establish the presence of resins in caoutchouc by ozonisation in carbon tetrachloride solution, and the operation may be made quantitative, since the resin is quantitatively converted into the ozonide. The ozonide obtained by direct solution and ozonisation of dammar resin was not uniform, and the resin was therefore subjected to a preliminary treatment with acetic acid and precipitation with water. All the resins investigated yielded solid ozonides, the m. p.'s of which lay between 53° and 81°.

The solubility of the ozonides was less than that of the resins; they are very sparingly soluble in light petroleum, slightly so in carbon tetrachloride, and yield clear solutions in alcohol, ethyl acetate, acetone, and acetic acid. The fission products are almost insoluble in light petroleum, slightly soluble in carbon tetrachloride, soluble in alcohol, ethyl acetate, acetone, and acetic acid, and, for the most part, in chloroform. A definite phytosterol—or *isocholesterol*—reaction is not given by the resins, ozonides, or their fission products. The iodine numbers of the ozonides, fission products, and resins are 126—285, 112—238, and 5—152 respectively. The ozonides have C=47—61%; H=6—11%; the fission products, C=60.8—69%; H=8—10%. The resins may be classified in the following groups: (i) Dammar, mastic, sandarac; (ii) brown and pale dammar copal, recent and fossil kauri copal; (iii) caoutchouc resin and guttapercha resin; (iv) French colophonium, American resin, Mark B, elemi, and galipot. The solubilities of dammar, mastic, and sandarac are very different, those of their ozonides and fission products closely similar. Eighty-two to 83% of dammar resin is soluble in acetic acid; the residue, after solution in light petroleum and precipitation with acetic acid, forms a white, amorphous mass, m. p. 211°, which probably consists of a hydrocarbon, $(C_{10}H_{16})_{16}$. The solubilities of the resins, ozonides, and fission products of the two dammar copals are approximately the same, and this is also true for the kauri copals. M. p.'s of the ozonides, 64° and 68°, 53° and 51° respectively; m. p.'s of resins, 154° and 158°, 92° and 119° respectively. Acid numbers, 198 and 201, 131 and 126 respectively. The solubilities of the resins, ozonides, and fission products of the members of the third group show almost exact agreement. M. p.'s of ozonides, 63° and 70°; m. p.'s of fission products, 92° and 87°. The resins, ozonides, and fission products of group IV also show marked analogies with respect to solubility, etc., for the fuller details of which the original memoir must be consulted.

H. W.

Synthesis of Santene. GUST. KOMPPA and S. V. HINTIKKA (*Bull. Soc. chim.*, 1917, [iv], 21, 13—19. Compare A., 1912, i, 279).—The authors now show that the hydrocarbon obtained from camphenyl chloride by the action of aniline, diethylaniline, or alcoholic potassium hydroxide (*loc. cit.*), is really a mixture, of which only a small proportion is camphenilene, the main product being santene, b. p. 140—141°, the properties of which agree well with those of natural santene. Further, that *isocamphenilol* is identical with santenol (Semmler's π -norborneol) and *isocamphenilone* with santenone (Semmler's π -norcamphor).

Camphenilol can also be converted into the corresponding hydrocarbon mixture by heating it with anhydrous sodium hydrogen sulphate for one hour at 190—200°.

W. G.

Ammonium Soaps of Colophony. LUDWIG PAUL (*Seifenfabrikant*, 36, 545—546, 567—569; from *Chem. Zentr.*, 1916, ii, 906—907).—An alcoholic solution of colophony solidifies to a stiff jelly when poured into dilute ammonia. Larger quantities are conveniently prepared by grinding γ -pinic acid (KS-acid) with

distilled water and treatment with ammonia in excess. The ammonium soap thus prepared greatly resembles the γ -sodium resin soap. Both form additive compounds with petroleum (compare A., 1915, i, 1066). Aqueous solutions of both resin soaps can be boiled without decomposition; on the other hand, decomposition is always observed with the γ -ammonium soap if this has been prepared with relatively little ammonia. If a concentrated alcoholic solution of colophony is poured into very dilute aqueous ammonia, a solution is obtained which deposits some resinous matter on boiling, and forms a milky emulsion, from which unchanged γ -pinic acid, m. p. 74—76°, is obtained by filtration or by hydrochloric acid. α -Pinic acid, m. p. 101—103°, is formed by addition of hydrochloric acid to the filtrate. Similar precipitates, m. p. about 93°, are obtained when preserved "KS" or colophony powder is treated with ammonia. "KS-acid" does not invariably melt at 76°, but often between 85° and 88°. A resin acid, m. p. 85—87°, is obtained from the calcium salts contained in the filtrate from the precipitation of γ -sodium resin soap by water containing calcium as well as by decomposition of the non-gelatinised ammonium soap. Further, γ -pinic acid, m. p. 85—87°, is obtained from γ -sodium resin soap by means of ether. The higher m. p. is attributed to the entrance of calcium into the resin and its non-removal by hydrochloric acid. A transparent piece of colophony yields the sodium resin soap with sodium hydroxide, from which γ -pinic acid, m. p. 75—76.5°, can be separated. If the latter is washed with much conductivity water the m. p. rises to 85—87°. Further, a substance, m. p. 85—87°, was obtained by the investigation of a two and a-half years old specimen of γ -pinic acid, which, in contrast to the former substance, was soluble in water. γ -Pinic acid gradually becomes transformed into α -pinic acid. Similarly, in the course of time, α -pinic acid is converted into β -pinic acid, m. p. 122—123°. The autoxidation of colophony is to be compared with the conversion of α -pinic acid into the β -compound. This is shown not only by the crumbling of colophony to powder (consisting chiefly of β -pinic acid), but also by the fact that α -pinic acid, m. p. 100—105°, passes within a short period into the β -compound. The α - and β -acids can be separated by the ammonia method, since the ammonium salt of the α -acid is readily decomposed whilst the β -compound shows little or no instability. γ -Pinic acid, the m. p. of which had risen from 74—77° to above 100° during two and a-half years, was stirred with water and ammonia, when a separation of γ -ammonium resin soap was not observed. Before being boiled, the solution deposited considerable quantities (18 grams from 35 grams) of a plastic mass (Kpl), m. p. 95—98°. The filtrate was treated with hydrochloric acid and the precipitate dissolved in conductivity water. Hydrochloric acid precipitated β -pinic acid, m. p. about 120°, from the extracts, so that the substance directly precipitated with ammonia is to be regarded as fairly pure β -pinic acid. Colophony is similarly decomposed with separation of "Kpl." In the "Kpl-substance" a resinous matter intermediate between α - and γ -pinic acids is present (in addition to α -acid), which possibly represents the first product of transformation. Colophony which had been treated

with nitric acid showed the same decomposition when treated with ammonia and boiled; the filtrate also contained β -pinic acid, the latter being characterised by its solubility in water and the formation of fluorescent, resin-lake solutions. Colophony is changed in a few hours by nitric acid in the same manner as by exposure to air for years. This transformation of colophony is attributed to the action of colloiddally contained water. On the other hand, colophony can decompose owing to loss of water. Whereas sylvic acid is formed by the action of cold alcohol, hot alcohol causes the formation of γ -abietic acid. Resinous substances may be classified into those soluble in petroleum (γ -pinic acid, sylvic acid, γ -abietic acid) and those insoluble in petroleum (Kpl., α - and β -pinic acids), but the classification is not final.

H. W.

Synthesis of Phenol Glucosides. EMIL FISCHER and LUKAS VON MECHTEL (*Ber.*, 1916, 49, 2813—2820).—Many glucosides of the phenols have been obtained in the past by the action of the dry sodium compound on acetobromoglucose in ethereal solution. A new process has now been developed, which consists in warming acetobromoglucose with the phenol in the presence of quinoline, and whereas β -glucosides were always formed in the old way, α -glucosides are produced as well by the new.

Thus, acetobromoglucose (50 grams), phenol (160 grams), and quinoline (19 grams) are heated on the water-bath for an hour or so, the base is extracted with dilute sulphuric acid and ether, and the excess of phenol is removed by heating at $100^{\circ}/0.2$ mm. The residue is a mixture of α - and β -glucosides, which are separated by crystallisation from carbon tetrachloride. Tetra-acetyl- β -phenol-glucoside is sparingly soluble in the cold, and is deposited in an almost pure condition, $[\alpha]_D^{20} - 28.94^{\circ}$; it may be hydrolysed by barium hydroxide solution to β -phenol-*d*-glucoside, $2H_2O$, m. p. $175-176^{\circ}$ (corr.), $[\alpha]_D^{20} - 71.9^{\circ}$, in the usual way (compare Fischer and Armstrong, A., 1901, i, 671).

Tetra-acetyl- α -phenol-glucoside is present in the same amount in the mother liquor; it has m. p. 115° (corr.), $[\alpha]_D^{20} + 164.9^{\circ}$ (benzene), and the corresponding α -phenol-*d*-glucoside crystallises with $1H_2O$ in slender needles, m. p. $173-174^{\circ}$ (corr.), $[\alpha]_D^{20} + 180^{\circ}$.

The rate of hydrolysis of these glucosides was compared with that of α -methylglucoside under the same conditions, and it was found that during the time that 4.5% of the latter is hydrolysed, 32% of the β -phenolglucoside and 68% of the α -phenolglucoside are hydrolysed. The remarkable feature of this result is not that the phenolglucosides are so easily hydrolysed, but that the β -form is more quickly changed than the α -isomeride, which is the reverse of what obtains with the methylglucosides.

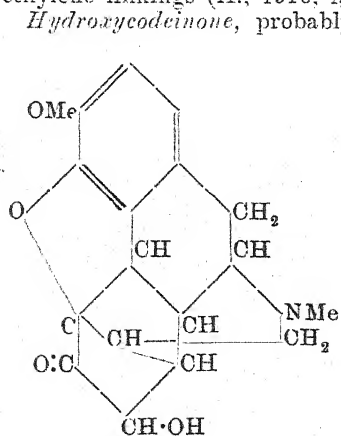
The β -phenolglucoside is hydrolysed by emulsin, but not by yeast extract; the α -glucoside behaves in the opposite way.

J. C. W.

The Cinchona Alkaloids. XVII. Degradation of Cincholeupone to 4-Aminomethyl-3-ethylpiperidine. PAUL RABE [with RICHARD PASTERNAK] (*Ber.*, 1916, 49, 2753—2756).—In

his last papers (1913) the author had foreshadowed further developments in the chemistry of the scission products of the cinchona alkaloids, including the partial synthesis of the bases by combining cincholeupone with various cinchonic or quinic acids, and he complains of Kaufmann's competition in this field (see this vol., i, 50). He now describes the conversion of cincholeupone (3-ethylpiperidine-4-acetic acid) through the ester into the *hydrazide*, colourless needles, m. p. 115° , then into the azide, and finally through the urethane or carbamide, into 4-aminomethyl-3-ethylpiperidine, which is a colourless base, b. p. $110^{\circ}/12$ mm., and forms a *diplatinichloride*, $B_2H_2PtCl_6 \cdot H_2O$, orange needles, decomp. 255° , and a *di-aurichloride*, $B_2HAuCl_4 \cdot H_2O$, golden leaflets, decomp. 205° .
J. C. W.

Thebaine. VI. Transformation of Thebaine into Hydroxycodeinone and its Derivatives. MARTIN FREUND and EDMUND SPEYER (*J. pr. Chem.*, 1916, [ii], 94, 135—178).—The connexion between thebaine and codeine has been demonstrated in various ways by Knorr and his colleagues on the one hand and in Freund's laboratory on the other (see A., 1903, i, 849; 1906, i, 303, 449). It has now been found that when thebaine, dissolved in boiling acetic acid, is treated with 30% hydrogen peroxide, or is oxidised by potassium dichromate and sulphuric acid, it is converted into a hydroxylic ketone which contains one oxygen atom more and a methylene group less than the original substance. It is not the amine-oxide formed under slightly different conditions (A., 1911, i, 76), because it is indifferent to the action of sulphurous acid, but a hydroxycodeinone, for it yields the same oxime as bromocodeinone (A., 1906, i, 303). Many derivatives of this compound are described, and the constitution of them is discussed at some length on the basis of Knorr's formula and the more preferable one recently proposed, which contains no aliphatic ethylene linkings (A., 1916, i, 738).



Hydroxycodeinone, probably of the annexed formula, crystallises in tablets, decomp. 275° , and forms a *hydrochloride*, columns, decomp. 285 — 286° , and the above-mentioned oxime, decomp. 279 — 280° . The *methiodide*, small prisms, decomp. 247° , can be demethylated in the usual way, and the *methiodide* of the secondary base so formed, leaflets, decomp. 267° , also loses trimethylamine readily enough, without, however, yielding a crystallisable nitrogen-free compound.

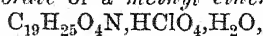
The *acetate* crystallises in elongated tablets, m. p. 185 — 186° , forms a *hydrochloride*, decomp. 258° , and an *oxime*, $1H_2O$, small

prisms, m. p. 148° , and reacts with cyanogen bromide to form *cyanonorhydroxycodeinone*, [$N\cdot CN$ instead of NMe in the above formula], which is a weak base and separates in well-developed tablets, m. p. 255° . The *benzoate* crystallises in columns, m. p. $245-247^{\circ}$.

When hydroxycodeinone is boiled with 30% hydrogen peroxide it is oxidised to the amine-oxide [$NMe\cdot O$], which forms a *picrate*, in small, rhombic crystals, decomp. $187-188^{\circ}$. Other attempts to degrade the compound by oxidation were fruitless, but three different products have been obtained by reduction. With zinc dust and formic acid the ketone group is attacked, and *hydroxycodeine* results, in prismatic rods, m. p. 293° . This is insoluble in sodium hydroxide, and forms a *hydrobromide*, decomp. 290° , and a *monoacetate*, leaflets, decomp. 283° . Stannous chloride apparently opens the oxide ring, with the formation of the yellow, phenolic *hydroxythebainone*, which yields a *hydrochloride*, stout columns, decomp. above 280° , and an *oxime*, decomp. 255° . On the other hand, the ketone-alcohol nature of the base is preserved when catalysed hydrogen or sodium hyposulphite is used as the reducing agent. In this case, one of the links in the "bridge" (across the ring at the bottom of the formula) disappears. The *hydroxydihydrocodeinone* so formed crystallises in elongated, jagged columns, m. p. $218-220^{\circ}$, and yields a *hydrochloride*, m. p. $268-270^{\circ}$, $[\alpha]_D -125.2^{\circ}$, in water; a *hydriodide*, m. p. $189-190^{\circ}$; the *hydrochloride* of an *oxime*, decomp. $275-278^{\circ}$; a *phenylhydrazone*, tablets, m. p. 204° ; an *acetate*, leaflets, m. p. $215-216^{\circ}$ (*hydrochloride*, decomp. 275° ; *oxime hydrochloride*, needles, m. p. $230-231^{\circ}$; free *oxime*, tablets, m. p. $179-180^{\circ}$); and a *benzoate*, m. p. $275-276^{\circ}$. A *tautomeride*, highly refractive scales, m. p. $219-220^{\circ}$, is formed if hydroxydihydrocodeinone is warmed with sodium amalgam and alcohol.

Although no product free from nitrogen could be obtained from hydroxycodeinone (see above), such can be realised in the case of hydroxydihydrocodeinone. The *methiodide*, stout prisms, decomp. 251° , yields a secondary base, stellar aggregates, m. p. 115° (*oxime*, lanceolate leaflets, m. p. $185-186^{\circ}$), the *methiodide* of which, leaflets, m. p. $255-256^{\circ}$, readily parts with trimethylamine to form "*hydroxydihydrocodeone*," $C_{17}H_{16}O_4$. This crystallises in rods, m. p. $214-215^{\circ}$, and forms an *oxime*, large spikes, m. p. 211° .

If hydroxydihydrocodeinone is reduced with sodium amalgam, or amalgamated zinc and hydrochloric acid, or by electrolysis at a lead cathode, then the oxide ring is ruptured and the corresponding *hydroxydihydrothebainone* is produced. This forms nodular groups, m. p. 145° , and yields a *hydrochloride*, decomp. 310° , $[\alpha]_D -52.47^{\circ}$, a *perchlorate*, decomp. 270° , an *oxime*, stout prisms, m. p. 222° , a *monoacetate*, m. p. 214° , insoluble in sodium hydroxide, and the *perchlorate* of a *methyl ether*,



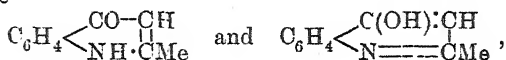
long columns, m. p. 134° .

Hydroxydihydrothebainone can also be indirectly degraded to a compound free from nitrogen. The *methiodide*, $1H_2O$, needles,

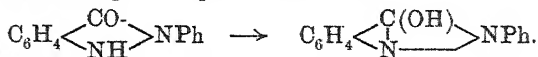
decomp. 210° , yields a secondary base, m. p. $242-243^{\circ}$, $[\alpha]_D -81.88^{\circ}$ (in dilute acetic acid) (*hydriodide*, quadratic tablets, m. p. 158°), but the methiodide of this is a resinous substance which, although it loses trimethylamine readily, does not give a definite product. If the secondary base is reduced with hydrogen and colloidal palladium, however, the resulting *demethylated hydroxytetrahydrothebaine*, $C_{19}H_{27}O_4N$, m. p. $239-240^{\circ}$, $[\alpha]_D -45.25^{\circ}$ (in dilute acetic acid) yields a *methiodide*, which loses trimethylamine readily and forms "7-hydroxytetrahydrothebaine," $C_{17}H_{26}O_4$, in groups of feathery needles, m. p. $143-144^{\circ}$.

If the treatment suitable to the oxidation of thebaine to thebaine oxide is prolonged (*ibid.*), a small quantity of *dehydrothebaine*, $C_{19}H_{19}O_3N$, is formed as well, in yellow prisms, m. p. $178-180^{\circ}$. The two methoxyl groups are intact in this, and the base forms a *methiodide*, tablets, decomp. 177° . J. C. W.

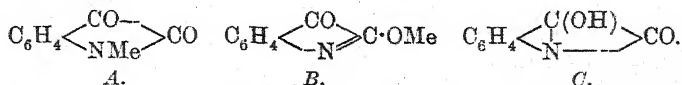
New Cases of Isomerism. GUSTAV HELLER (*Ber.*, 1916, 49, 2757—2774).—Lactams are usually regarded as substances which contain such a labile hydrogen atom that as a rule they only exist in one of the desmotropic forms. This is not always so, however, for the author has shown that the two isomerides represented by the formulæ



are distinct individuals (A., 1908, i, 913). A case of desmotropism seems to be exhibited, on the other hand, by 3-hydroxy-2-phenylindazole. A stable form of this is obtained by heating hydrazobenzene-*o*-carboxylic acid with acetic anhydride. It crystallises in colourless needles or rods, m. p. 204° , and forms a *benzoate*, long spikes, m. p. 180.5° , but it changes into the labile ketonic modification, m. p. 217° , by solution in phosphoryl chloride. This is transformed into the hydroxylic form by successive crystallisations, and it is the modification which Freundler has described (A., 1907, i, 158). The change is represented thus:



A particularly interesting case of the wandering of a hydrogen atom is furnished by isatin. The lactam and lactim forms of this have long been known in the methyl compounds A and B. The remaining alternative, C, which is designated "isatol," has now been isolated:



This is obtained as follows: Isatin, dissolved in hot alcohol, is shaken with silver acetate solution, when the N-silver salt separates at once as a greyish-red powder, which gives a deep bluish-red solution in pyridine. This silver salt is warmed with benzoyl chloride

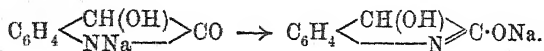
and benzene, the silver chloride is removed, and the filtrate left to crystallise. Isatol separates, and is purified ultimately by crystallisation from methylal. *Isatol* forms red prisms, m. p. 194.5°, is insoluble in sodium carbonate or ammonia, but soluble with orange-red colour in sodium hydroxide. This solution becomes pale on heating, and then acids precipitate ordinary isatin. Acetic anhydride, benzoyl chloride, phenylhydrazine, sodium hydrogen sulphite, methyl iodide, and sodium nitrite have no action, but diazomethane gives the corresponding *methyl ether*, as a pale yellow, amorphous substance.

The function of the hydrogen atom in each of the three positions is therefore revealed. It has the most acidic properties in the imino-combination. The evidence in support of this is the fact that isatin dissolves in ammonia whereas isatol does not; isatin decomposes silver acetate, and the ethyl ether of the α -oxime (Baeyer, 1882) gives deep blue solutions in sodium hydroxide, whereas the ethyl ether of the β -oxime is only phenolic and gives a yellow solution. α -Isatoxime, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} > C:N \cdot OH$, is conveniently obtained by the action of hydroxylamine on *O*-methylisatin (A., 1907, i, 442). It changes into benzoylenecarbamide, $C_6H_4 \begin{smallmatrix} \text{CO-NH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$, on warming with sodium hydroxide.

The various salts of isatin and its ethers and oximes (see also *ibid.*) owe their differences of colour mainly to the different attachments of the metal, the N-salts being usually deeper in colour than the O-salts. The question whether the metallic atom is linked to nitrogen or oxygen or even to carbon should, therefore, be taken into account in other cases of salt formation, and several examples are discussed at length.

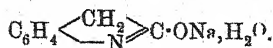
J. C. W.

Oxindole. GUSTAV HELLER [with HERMANN HEINE] (*Ber.*, 1916, 49, 2775—2778).—It has already been shown that dioxindole forms a violet salt which quickly changes into a colourless isomeride (A., 1904, i, 416). The change is most probably that of an N-salt into an O-salt, thus:



It has now been tested whether oxindole undergoes similar reactions, but the results obtained are obscure and inconclusive.

Oxindole is best obtained by reducing *o*-nitrophenylacetic acid with ammonia and ferrous sulphate. If sodium hydroxide and ferrous sulphate are used, the product is *o*-azoxyphenylacetic acid (Reissert, A., 1909, i, 51). Oxindole reacts with sodium ethoxide to form a colourless salt, probably of the formula

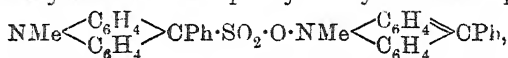


This reacts with benzoyl chloride to form the normal benzoate,

m. p. 192°, and also a *tribenzoyl* derivative, $C_6H_4 \begin{smallmatrix} \text{CBz}_2 \\ \text{NBz} \end{smallmatrix} \text{CO}$, tufts of pale yellow needles, m. p. 172–173°. J. C. W.

The so-called Chromoisomerism of Salts of Phenylmethylacridinium. F. KEHRMANN and KNUT STAHRFOSS (*Ber.*, 1917, 50, 24–30).—Just as the pure salts of 9-phenylacridine have all the same colour (A., 1916, i, 744), so the salts of phenylmethylacridine are all yellow, except the iodide, which is normally darker than the other haloids, and the sulphite, which exhibits various colours. Hantzsch has recently reinvestigated the sulphites (A., 1916, i, 836), but it is now claimed that his actual analytical data support Kehrman's views very fully, whilst the "theoretical" data were wrongly calculated. It is maintained that the supposed brown anhydride is a monohydrate, which necessitates a revision of the formulæ assigned to the various "solvates."

The authors recognise a yellow, very unstable, normal sulphite, $(CPh \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{NMe})_2\text{SO}_3$; a quinhydrone-like salt compounded of phenylmethylacridine and phenylmethylacridinesulphonic acid,

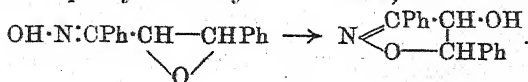


which is reddish-brown to olive-green, according to the amount and nature of the combined solvent; and the colourless alkali salts of this acid. J. C. W.

Compounds of Pyridine with the Alkali Metals. III. BRUNO EMMERT (*Ber.*, 1917, 50, 31–35. Compare A., 1916, i, 668).—When the sodium compound of pyridine, $C_5H_5\text{NNa}$, is treated with moist ether, a very readily oxidisable mixture of tetrahydridipyridyls is formed. The constitution of this is revealed by the nature of the products of auto-oxidation, one of them being 4:4'-dipyridyl, m. p. 111–112°, b. p. 302° (corr.), and the other a yellow, hydroxylic compound, $C_{10}H_{12}\text{ON}_2$ (or perhaps a hydrate of this), which yields 2:2'-dipyridyl, m. p. 69·5°, when heated with sulphuric acid at 280°. J. C. W.

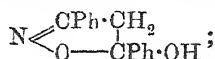
Action of Hydroxylamine and Hydrazine on Benzoylphenylethylene Oxide. OSKAR WIDMAN (*Ber.*, 1916, 49, 2778–2782. Compare A., 1916, i, 406).—The work of two of the author's colleagues on substituted benzoylphenylethylene oxides (following abstracts) has thrown more light on compounds of this class, and the earlier views with regard to the "oximes" and "hydrazone" are now modified.

The "γ-oxime" is apparently the true oxime, probably mixed with a stereoisomeride, the "δ-oxime." It changes very readily into the so-called "α-oxime," m. p. 169–169·5°, which is really 4-hydroxy-3:5-diphenyl-4:5-dihydroisooxazole, thus:



This forms an *acetate*, in leaflets, m. p. 175—176°, when boiled with acetic anhydride and a drop of sulphuric acid for a few moments. A characteristic reaction of these ethylene oxides is that they liberate iodine when boiled with glacial acetic acid and potassium iodide. The " γ -oxime" does this, but not the " α -oxime."

The so-called " β -oxime," m. p. 161°, is perhaps a stereoisomeride of the *isooxazole*, " α ." A further isomeride can be obtained by boiling the chlorohydrin of benzoylphenylethylene oxide with excess of alcoholic hydroxylamine hydrochloride. The chlorohydrin is now recognised to be β -chloro- β -benzoyl- α -phenylethyl alcohol, $\text{CHClBz}\cdot\text{CHPh}\cdot\text{OH}$, and the new hydroxylamine derivative is therefore 5-hydroxy-3:5-diphenyl-4:5-dihydroisooxazole,



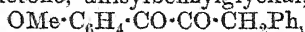
it crystallises in leaflets, m. p. 173°, and changes into diphenylisooxazole on heating with acetic anhydride and a drop of sulphuric acid.

The so-called "hydrazone," m. p. 209°, is really 4-hydroxy-3:5-diphenylpyrazoline, $\text{N} \begin{array}{c} \text{CPh}\cdot\text{CH}\cdot\text{OH} \\ \diagdown \quad | \\ \text{NH}\cdot\text{CHPh} \end{array}$, for it yields a nitroso-compound, in yellow pyramids or needles, m. p. 155° (decomp.).

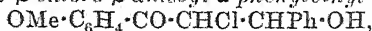
J. C. W.

Anisoylphenylethylene Oxide. HENRIK JÖRLANDER (*Ber.*, 1916, 49, 2782—2795).— ω -Chloro-*p*-methoxyacetophenone condenses with benzaldehyde in the presence of sodium ethoxide, like the simple ω -chloroacetophenone (*A.*, 1913, i, 1220), to form anisoylphenylethylene oxide, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH} \begin{array}{c} \text{CHPh} \\ \diagdown \quad | \\ \text{O} \end{array}$, in

rhombic tablets, m. p. 82°. This can be converted into the corresponding yellow diketone, anisylbenzylglyoxal,



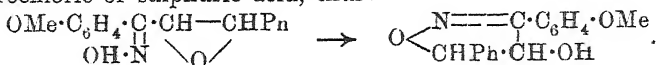
which will be described in a forthcoming paper. It forms two chlorohydrins. When covered with cold alcoholic hydrogen chloride, it yields β -chloro- β -anisoyl- α -phenylethyl alcohol,



in colourless prisms, m. p. 117°, the above diketone being formed at the same time. This chlorohydrin is reconverted into the oxide when treated with cold sodium ethoxide solution, and it forms an *acetate* which crystallises in leaflets, m. p. 72°. When the oxide is treated with acetyl chloride in moist acetic acid, or with hydrogen chloride in benzene solution, β -chloro- α -anisoyl- β -phenylethyl alcohol is formed, in small needles, m. p. 110°. This yields the above diketone when treated with sodium ethoxide solution, forms an *acetate*, m. p. 84°, and may be oxidised to a diketone, which condenses with *o*-phenylenediamine to give 2- α -chlorobenzyl-

anisylquinoxaline, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{CHPhCl}\cdot\text{C}\cdot\text{N} \end{array} \text{C}_6\text{H}_4$, m. p. 92—93°.

Anisoylphenylethylene oxide gives an *oxime*, leaflets, m. p. 125—126°, when left with hydroxylamine hydrochloride and sodium acetate (2 mols. each); this changes into 4-hydroxy-5-phenyl-3-anisyl-4:5-dihydroisooxazole, slender needles, m. p. 150°, in alkaline solutions or on warming with alcohol and a drop of hydrochloric or sulphuric acid, thus:



This compound is also obtained by leaving an alcoholic solution of the oxide with hydroxylamine hydrochloride (2 mols.) or by boiling the chlorohydrin, m. p. 110°, with hydroxylamine hydrochloride; its *acetate* has m. p. 128°. The isomeric 5-hydroxy-5-phenyl-3-anisyl-4:5-dihydroisoxazole, glistening leaflets, m. p. 185°, is obtained in the same way from the other chlorohydrin, m. p. 117°, or by boiling an alcoholic solution of the oxide with hydroxylamine hydrochloride (3 mols.); its *acetate* has m. p. 152—153°. If, in the last reactions, the action of hydroxylamine is prolonged, 4-oximino-5-phenyl-3-anisyl-4:5-dihydroisooxazole, $\text{O} \begin{array}{c} \text{N} \\ \text{CHPh} \end{array} \begin{array}{c} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ \text{C} \cdot \text{N} \cdot \text{OH} \end{array}$, is also formed, in colourless, microscopic needles, m. p. 225° (decomp.).

When boiled with alcoholic hydrazine hydrate, anisoylphenylethylene oxide forms 4-hydroxy-5-phenyl-3-anisylpyrazoline, $\text{NH} \begin{array}{c} \text{N} \\ \text{CHPh} \end{array} \begin{array}{c} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ \text{CH} \cdot \text{OH} \end{array}$ in colourless needles, m. p. 176—177° (decomp.), the *diacetyl* derivative of which has m. p. 195—196°. The base forms a *nitroso*-compound, yellow needles, m. p. 148° (decomp.), which yields an *acetate*, pale yellow prisms, m. p. 177° (decomp.), and gives rise to 5-phenyl-3-anisylpyrazole on boiling with glacial acetic acid or alcoholic alkali hydroxide. This crystallises in needles, m. p. 159—160°, and forms an *acetyl* derivative, m. p. 88°.

Anisoylphenylethylene oxide also reacts with phenylhydrazine in boiling acetic acid, yielding 1:5-diphenyl-3-anisylpyrazole, in long needles, m. p. 140°, which readily forms a bromine compound, $\text{C}_{22}\text{H}_{17}\text{ON}_2\text{Br}$, m. p. 149°. With an excess of phenylhydrazine in cold acetic acid, however, the product is α -hydroxy- β -N^c-phenylhydrazinoethyl anisyl ketone phenylhydrazone,

$\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{N} \cdot \text{NHPh}) \cdot \text{CH}(\text{OH}) \cdot \text{CHPh} \cdot \text{NPh} \cdot \text{NH}_2$, which crystallises in needles, m. p. 166° (decomp.), and readily suffers condensation to 3-anisyl-1:5-diphenylpyrazole. It forms a *nitroso*-compound,

$\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{N} \cdot \text{NHPh}) \cdot \text{CH}(\text{OH}) \cdot \text{CHPh} \cdot \text{NPh} \cdot \text{NO}$, in pale yellow leaflets, m. p. 156—157° (decomp.), and a *benzylidene* compound, m. p. 141°, and reacts with bromine to give a *compound*, $\text{C}_{22}\text{H}_{15}\text{ON}_2\text{Br}_2$, m. p. 165—166°. J. C. W.

Aromatic Oxido-compounds. [Ethylene Oxides]. SVEN BONFORSS (*Ber.*, 1916, 49, 2795—2813. Compare preceding abstracts).—The condensation of aldehydes with ω -bromoaceto-

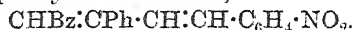
phenone is not a general reaction, but the presence of a halogen atom or nitro-group in the nucleus is distinctly favourable to the production of substituted ethylene oxides. *m*-Nitrobenzaldehyde reacts particularly well, and many properties of the benzoyl-*m*-nitrophenylethylene oxide so formed are now described.

Benzoyl-m-nitrophenylethylene oxide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{array}{c} \text{CHBz} \\ \diagup \text{O} \end{array}$, crystallises from alcoholic solutions when these are slowly cooled in shimmering, prismatic leaflets, or when quickly cooled in long, matted needles, m. p. 118°. *Benzoyl-p-nitrophenylethylene oxide* forms leaflets, m. p. 148°. *Benzoyl-p-chlorophenylethylene oxide* crystallises in large, thin tablets, m. p. 79–80°. *Benzoyl-p-isopropylphenylethylene oxide* has m. p. 76°, and slowly suffers oxidation to benzoylformic acid and cumenaldehyde.

These ethylene oxides can be made to condense again with ω -bromoacetophenone to form butadiene dioxides. Thus, in the last preparation, some α -benzoyl- β -phenyl- δ -p-isopropylphenyl-
 $\text{CHBz} \cdot \text{CPh} \cdot \text{CH} \begin{array}{c} \diagup \text{O} \end{array} \cdot \text{CH} \begin{array}{c} \diagup \text{O} \end{array} \cdot \text{C}_6\text{H}_4 \text{Pr}^\beta$
butadiene dioxide, , silky needles,

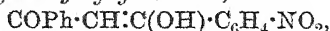
m. p. 129°, is formed, as well as the simple oxide. α -Benzoyl- β -phenyl- δ -p-nitrophenylbutadiene dioxide crystallises in shimmering leaflets, m. p. 207° (corr.), and α -benzoyl- β -phenyl- δ -p-chlorophenylbutadiene dioxide has m. p. 171°.

The oxides readily lose oxygen and change into ethylenes when warmed with glacial acetic acid and potassium iodide. Thus, benzoyl-*m*-nitrophenylethylene oxide yields phenyl *m*-nitrostyryl ketone, and the corresponding butadiene dioxide gives α -benzoyl- β -phenyl- δ -p-nitrophenyl- $\Delta^{\alpha\gamma}$ -butadiene,

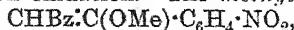


This exists in a sparingly soluble form, pale yellow crystals, m. p. 251° (corr.), and in a very soluble modification, m. p. 215° (corr.), which is rose-red if prepared in the dark, but becomes lemon-yellow in the light, and changes into the less fusible isomeride when boiled with glacial acetic acid. α -Benzoyl- β -phenyl- δ -p-chlorophenyl- $\Delta^{\alpha\gamma}$ -butadiene also exists in a more stable, sparingly soluble form, m. p. 263° (corr.), and in a labile form, m. p. 190° (corr.).

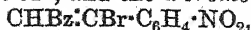
An isomeride of benzoyl-*m*-nitrophenylethylene oxide, namely, phenyl *m*-nitro- α -hydroxystyryl ketone,



can be obtained by the gradual addition of potassium hydroxide to a boiling methyl-alcoholic solution of $\alpha\beta$ -dibromo- β -*m*-nitrophenylpropiofenone, the product of the action of bromine on *m*-nitrophenyl styryl ketone. The compound crystallises in pale yellow, coral-like aggregates, m. p. 135°, titrates as a pure enol, forms a copper salt, and yields *m*-nitrobenzoic acid and benzoylformic acid on oxidation. The methyl ether,



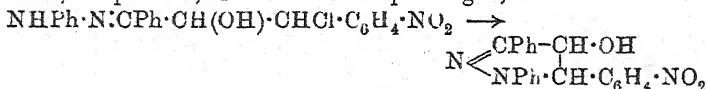
matted filaments, m. p. 91°, and the α -bromo-compound,



long needles, m. p. 97—98°, are also formed in this reaction, and by suitably arranging the conditions they can be made the chief products.

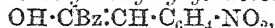
Benzoyl-*m*-nitrophenylethylene oxide and its enolic isomeride react with hydrazine hydrate to form 3-phenyl-5-*m*-nitrophenyl-pyrazole, $N \begin{smallmatrix} \text{CPh} \cdot \text{CH} \\ \text{NH} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \end{smallmatrix}$, m. p. 205°, which is feebly basic and yields an *acetyl* derivative, m. p. 156°. Similarly, phenylhydrazine gives rise to 1:3-diphenyl-5-*m*-nitrophenylpyrazole, yellow, hexagonal prisms, m. p. 131—132°, which may also be prepared by the action of boiling alcoholic silver nitrate solution on the corresponding pyrazoline, $N \begin{smallmatrix} \text{CPh} \cdot \text{CH}_2 \\ \text{NPh} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \end{smallmatrix}$, a dark red compound, m. p. 149°, which is obtained by boiling phenyl *m*-nitrostyryl ketone with phenylhydrazine and acetic acid (compare Auwers and Voss, A., 1910, i, 70).

The chlorohydrin of the ethylene oxide, β -chloro- α -benzoyl- β -*m*-nitrophenylethyl alcohol, $\text{OH} \cdot \text{CHBz} \cdot \text{CHCl} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, m. p. 100—100.5°, is obtained by the action of dry hydrogen chloride on a suspension of the oxide in carbon tetrachloride and chloroform. It forms unstable *additive* compounds with solvents; for example, with 3EtOH, with 1MeCO₂H, and 1CCl₄. The *benzoate* has m. p. 147°. With phenylhydrazine it forms a true *phenylhydrazone*, pale yellow cubes, m. p. 104°, which changes into 4-hydroxy-1:3-diphenyl-5-*m*-nitrophenylpyrazoline, long, orange needles, m. p. 200°, if the action is prolonged, thus:



This reacts with benzoyl chloride in cold pyridine to form the *O*-benzoate, m. p. 156—157°, but when warmed with the agent it loses water and changes to the above pyrazole, m. p. 131—132°.

The chlorohydrin is reconverted into the oxide when treated with alcoholic alkali hydroxide, but it loses hydrogen chloride in the other possible way when heated at 80° under reduced pressure, forming phenyl *m*-nitro- α -hydroxystyryl ketone,



in pale yellow prisms, m. p. 118°. This behaves as an $\alpha\beta$ -diketone, forming with *o*-phenylenediamine 2-phenyl-2-*m*-nitrobenzylquinazoline, long, felted needles, m. p. 121—122°, and suffering the benzil transformation to phenyl-*m*-nitrobenzylglycolic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CPh}(\text{OH}) \cdot \text{CO}_2\text{H}$, long needles, m. p. 166—167°.

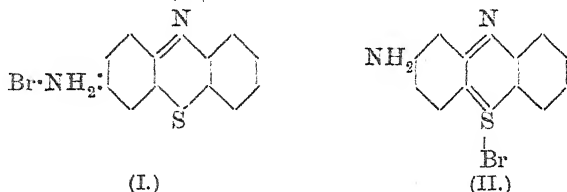
J. C. W.

Vat Dyes. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (U.S. Pat., 1209163; from *J. Soc. Chem. Ind.*, 1917, 36, 211).—Vat dyes are obtained by heating para-quinones with arylaminoacetic acids in a suitable solvent. The substance, $\text{NMePh} \cdot \text{C}_6\text{H}_2\text{O}_2 \cdot \text{NMePh}$, brown, crystalline powder, m. p. 232° (decomp.), is specially claimed. It yields a colourless vat with alkaline hyposulphite, from which it gives yellow tints on animal fibres.

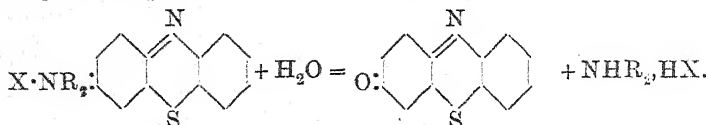
H. W.

Dyes of the Methylene-blue Group. III. Moderated Action of Aliphatic Amines on Phenazthionium Salts. F. KEHRMANN [with ADRIEN ROBERT and MAURICE SANDOZ] (*Ber.*, 1916, 49, 2831—2838. Compare A., 1916, i, 435, 673).—In the earlier papers it was shown that amines can react with phenazthionium salts, especially the perbromide, to give dyes of the methylene-blue series. Under some conditions the reaction can be so modified that only one amino-group is introduced.

Thus, if phenazthionium perbromide is triturated with alcoholic ammonia an orange solution of a thiazime is obtained. If this is allowed to evaporate and the residue is dissolved in water and mixed with sodium bromide, thiazime bromide (I) is deposited, but if the solution is acidified first and then treated in the same way, a more greenish-blue product is obtained, which apparently contains the isomeride (II):



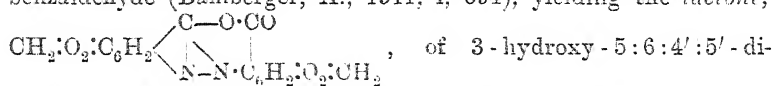
Similarly, if an alcoholic solution of dimethylamine is added to a suspension of the perbromide in ether and alcohol until a bluish-violet solution is obtained, and the further action of the base is stopped by neutralisation, the following substances are produced: bromophenazthione, which is soluble in ether; *dimethylthiazime*, which can be precipitated as the *perchlorate* in very long, bronzy needles, or as the violet *platinichloride*; reddish-violet methylthiazime (?), which can be extracted by ether from an alkaline solution (sodium carbonate) and forms a dark violet-brown perchlorate; and methylene-blue. Diethylamine behaves in the same way; *diethylthiazime perchlorate* forms long, metallic-looking, violet needles, and the *platinichloride* almost black granules with bronzy lustre. These alkylated thiazimes yield phenazthione on boiling with aqueous alkalis, thus:



The absorption spectra of solutions of the para-quinonoid mono-acid salts of six thiazimes were determined. The chief characteristic is the appearance of a band in the ultra-violet with a maximum at about $\lambda = 290 \mu\mu$. This seems to be a feature common to all tri-cyclic phenazthionium dyes (compare *ibid.*, 673). J. C. W.

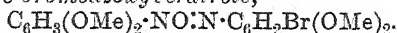
Azoxycatechol Ethers and Related Substances. GERTRUDE MAUD ROBINSON (*T.*, 1917, 111, 109—121).—4:5:4':5'-Dimethylenetetraoxyazobenzene-2:2'-dicarboxylic acid is obtainable

from 6-nitro-3:4-methylenedioxybenzoic acid, not only by heating with nitrobenzene (Robinson and Robinson, T., 1914, 105, 1466; A., 1916, i, 166), but also by treating with hot aqueous sodium or potassium hydroxide, in which case it is accompanied by *azoxy-piperonal*, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2(\text{CHO})\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_2(\text{CHO})\cdot\text{O}_2:\text{CH}_2$. This substance can also be produced by the action of sodium methoxide on nitropiperonal in methyl-alcoholic solution; it is changed by nitric acid into a *nitrodimethylenetetraoxyazoxybenzenecarboxylic acid*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2(\text{O}_2:\text{CH}_2)\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_2(\text{O}_2:\text{CH}_2)\cdot\text{NO}_2$, which is attacked by sodium hydroxide solution with formation of a colourless, crystalline substance giving a reddish-violet solution in aqueous sodium hydroxide, and of 2-nitro-4:5:4':5'-dimethylenetetraoxyazobenzene-2'-carboxylic acid. When heated alone, or with acetic acid or nitrobenzene, azoxy-piperonal behaves similarly to azoxybenzaldehyde (Bamberger, A., 1911, i, 694), yielding the *lactone*,



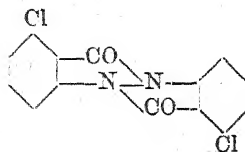
methylenetetraoxy-2-phenylindazole-2'-carboxylic acid, which on oxidation is converted into 4:5:4':5'-dimethylenetetraoxyazobenzene-2:2'-dicarboxylic acid.

The formation of an unsymmetrical nitro-compound on nitrating azoxy-piperonal led to further experiments on the nitration of *azoxy-veratrole*, in which it was found that in acetic acid solution only a mononitro-derivative, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{NO}_2$, was formed; similarly, bromination in acetic acid solution gave a monobromo-product, 6-bromoazoxyveratrole,



These results accord well with the unsymmetrical constitution of azoxy-compounds as originally suggested by Angeli. D. F. T.

A Method of Formation of 6:6'-Dichloro-2:2'-azobenzoic acid. S. REICH and W. MERKI (*Bull. Soc. chim.*, 1917, [iv], 21, 13).—When an aqueous alcoholic solution of 6-chloro-2-nitrobenzaldehyde (1 mol.) and potassium cyanide (5 mols.) is acidified at 0° with hydrochloric acid and, after one hour, heated on a water-bath, the *cyanohydrin*, $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CN}$, a yellow powder, m. p. 134—136°, is obtained. If, however, the acidified mixture is allowed to remain twenty-four hours and then heated on a water-bath with concentrated hydrochloric acid, the product is 6:6'-dichloro-2:2'-azobenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}_2\text{H}$, yellow needles, m. p. 248—250° (decomp.), which, when distilled with calcium oxide, gives 3:3'-dichloroazobenzene, m. p. 96°. If the acid



is reduced with stannous chloride or with hydrogen in the presence of palladium, a compound, $\text{C}_{14}\text{H}_6\text{O}_2\text{N}_2\text{Cl}_2$, pale yellow needles, m. p. 347—348°, is obtained, to which the constitution (annexed formula) is assigned. The proof of this constitution is given by the following series of reactions. *Ethyl 6:6'-dichloro-2:2'-azobenzoate*, yellow

low crystals, m. p. 125—126°, when reduced with hydrogen in the presence of palladium, gives *ethyl 6:6'-dichloro-2:2'-hydrazobenzoate*, colourless rhombohedra, m. p. 87—88°. When concentrated hydrochloric acid is added to an alcoholic solution of this ester, it yields the cyclic compound, m. p. 347—348°, described above.

W. G.

Azocarboxylic Acids. A. ANGELI (*Atti R. Accad. Lincei*, 1917, [v], 26, i, 95—101).—Owing to its analogy in form to nitroxyl, O:NH, the unstable phenyldi-imide, NPh:NH, should exhibit a similar series of reactions. It is, indeed, found that phenyldi-imide reacts readily with aromatic aldehydes, giving compounds of the type of *as*-benzoylphenylhydrazine: $R \cdot CHO + NPh:NH = OH \cdot CR:N \cdot NHPh = R \cdot CO \cdot NH \cdot NHPh$. To effect this reaction it is not necessary to make use of the pure phenylazocarboxylate, NPh:N·CO₂K (compare Widman, A., 1895, i, 603), since the liquid obtained by hydrolysing the amide, NPh:N·CO·NH₂, with dilute potassium hydroxide at a gentle heat serves equally well. When acetone is used in place of the aromatic aldehyde, no characteristic products are obtained.

This reaction is analogous to some extent with those in which the scission of the benzenesulphonic derivatives of hydrazine or phenylhydrazine take part (A., 1915, i, 847).

Oxidation of phenylazocarboxamide in acetic acid solution by means of hydrogen peroxide yields a *compound*, which forms pale yellow needles decomposing at 151°, and appears to be one of the two azoxy-derivatives, O:NPh:N·CO·NH₂ and NPh:NO·CO·NH₂, corresponding with the original azo-compound, NPh:N·CO·NH₂.

T. H. P.

Formation of *m*-Nitrophenylhydrazine from *m*-Nitroaniline by Bischler and Brodsky's Method. A. W. VAN DER HAAR (*Chem. Weekblad*, 1917, 14, 147—148).—The low yield of *m*-nitrophenylhydrazine is due to the great solubility of the intermediate products. The difficulty can be overcome by saturating the liquid with sodium chloride.

A. J. W.

Isomeric Hydrazones of Glyoxylic Acid. M. BUSCH, FRIEDR. ACHTERFELD, and RUD. SEUFERT (*J. pr. Chem.*, 1915, [ii], 92, 1—39. Compare Busch and Meussdörffer, A., 1907, i, 347).—It has already been shown that the *o*-bromophenylhydrazone of glyoxylic acid can exist in two forms (*loc. cit.*), and the authors now describe the conditions under which it is generally possible to favour the formation of either modification of a substituted phenylhydrazone of this acid. The isomeric modifications of any arylhydrazone have very different solubility in benzene, the sparingly soluble variety being described as the α -isomeride and the more soluble as the β -form. If interaction between dichloroacetic acid and the arylhydrazone occurs in presence of alkali carbonate or hydrogen carbonate, the sparingly soluble α -form preponderates in the product, but with an excess of alkali hydroxide the proportion

of the β -compound is greatly increased. Substitution in the meta- or para-position of the phenylhydrazine exerts no important influence on the progress of the reaction, but if the ortho-position is occupied the result shows an increase in the percentage of the β -product. The isomerism of the hydrazones extends to their salts, esters, and benzoyl derivatives, but acetic anhydride appears to exert a disturbing influence on the β -compounds, only one set of acetyl derivatives being obtainable. The β -compounds are more strongly acidic than the α -isomerides, and it appears most probable that the existence of the isomerides is due to stereoisomerism,

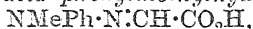
representable by the formulæ $\begin{array}{c} \text{H} \cdot \text{C} \cdot \text{CO}_2\text{H} \\ | \\ \text{N} \cdot \text{NHR} \end{array}$ and $\begin{array}{c} \text{H} \cdot \text{C} \cdot \text{CO}_2\text{H} \\ | \\ \text{NHR} \cdot \text{N} \end{array}$ for the α - and β -compounds respectively. This view explains the relatively greater acidity of the β -isomerides and the favourable influence of hydroxyl ions on their formation; it is also in agreement with the greater stability of the esters of the β -forms.

α -Glyoxylic acid phenylhydrazone, m. p. 138° , has already been obtained by the interaction of dichloroacetic acid and phenylhydrazine in the presence of alkali carbonate (Busch and Meussdörffer, *loc. cit.*; Elbers, A., 1885, 534). In the presence of excess of alkali hydroxide the product contains the former compound accompanied by the β -isomeride, yellow needles, m. p. 128 — 129° (decomp.), which can be separated by its ready solubility in benzene. The β -hydrazone dissolved in methyl-alcoholic sulphuric acid undergoes transformation into the α -isomeride, which further undergoes partial esterification. Both isomerides form salts with alkalis; the α -isomeride yields a *potassium* salt, yellow crystals; a sodium salt, $\text{C}_6\text{H}_7\text{O}_2\text{N}_2\text{Na}$, colourless leaflets, decomp. near 250° ; a sparingly soluble sodium salt, $\text{C}_8\text{H}_7\text{O}_2\text{N}_2\text{Na} \cdot \text{C}_8\text{H}_5\text{O}_2\text{N}_2$; an ammonium salt, $\text{C}_8\text{H}_7\text{O}_2\text{N}_2\text{NH}_4$, prisms, m. p. near 175° (decomp.), and a sparingly soluble ammonium acid salt, yellow leaflets; the β -isomeride forms a *sodium* salt, $\text{C}_8\text{H}_7\text{O}_2\text{N}_2\text{Na}$, m. p. indistinct near 273° (decomp.), more soluble than the corresponding salt of the α -compound.

The following phenylhydrazones of glyoxylic acid were prepared in the same manner as the preceding, with the exception that alcohol was added for the purpose of dissolving the arylhydrazine.

Glyoxylic acid m-4-xylylhydrazone, $\text{C}_6\text{H}_4\text{Me}_2 \cdot \text{NH} \cdot \text{N} : \text{CH} \cdot \text{CO}_2\text{H}$; α -compound, yellow leaflets, m. p. 125 — 126° (decomp.); β -compound, yellow needles, m. p. 110° (decomp.); the *sodium* salt of each consisted of yellow leaflets; the β -compound could be converted into the α -isomeride by the action of methyl-alcoholic sulphuric acid at the ordinary temperature for four hours. *Glyoxylic acid m-2-xylylhydrazone*; α -compound, pale yellow, cubical crystals, m. p. 142 — 144° (decomp.); β -compound, sulphur-yellow needles, m. p. 115 — 117° (decomp.). *Glyoxylic acid ψ -5-cumylhydrazone*, $\text{C}_6\text{H}_4\text{Me}_3 \cdot \text{NH} \cdot \text{N} : \text{CH} \cdot \text{CO}_2\text{H}$; α -compound, yellow leaflets, m. p. 144 — 145° ; β -compound, greenish-yellow needles, m. p. 127° (decomp.). *Glyoxylic acid o-chlorophenylhydrazone*; α -form, yellow needles, m. p. 153 — 154° (decomp.); β -form, m. p. 142 — 143° (decomp.) (compare Busch and Meussdörffer, *loc. cit.*).

Glyoxylic acid *o*-bromophenylhydrazine in both forms has already been described (Busch and Meussdörffer, *loc. cit.*); the β -form can, as usual, be converted into the α -isomeride by the action of methyl-alcoholic sulphuric acid, the α -isomeride in part undergoing change into its *methyl* ester, needles, m. p. 139°; the α - and β -modifications of the *m*-bromophenylhydrazine, $C_6H_4Br \cdot NH \cdot N : CH \cdot CO_2H$, form yellow leaflets, m. p. 136—139°, and yellow needles, m. p. 122° respectively, whilst the α - and β -isomerides respectively of the *p*-bromophenylhydrazine form yellow needles, m. p. 137° (decomp.) (*benzoyl* derivative, yellow leaflets, m. p. 175—176°), and yellow leaflets, m. p. 121° (decomp.) (*benzoyl* derivative, yellow leaflets or needles, m. p. 123°). Glyoxylic acid *o*-iodophenylhydrazine; only the α -form was isolable (Busch and Meussdörffer, *loc. cit.*); *p*-iodophenylhydrazine; α -modification, orange-yellow needles, m. p. 155° (decomp.); β -isomeride, yellow needles, m. p. near 135° (decomp.). Glyoxylic acid phenylmethylhydrazine,

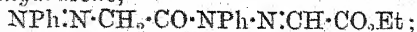


was obtained only in one form, probably of the β -constitution, colourless leaflets, m. p. 165—167° (decomp.); the corresponding phenylethylhydrazine (compare Elbers, A., 1885, 534) also was obtained in only one form.

Glyoxylic acid semicarbazone, m. p. 202—203° (compare Darapsky and Prabhakar, A., 1912, i, 841), and pyruvic acid phenylhydrazine appear not to yield stereoisomerides.

The semicarbazones of glyoxylic esters cannot be obtained by the interaction of the arylhydrazine with the alkyl dichloroacetate because of the necessity of the presence of alkali, and, as has been already mentioned, the action of alcohol and mineral acid on the two sets of isomerides yields the esters of the α -modifications only. For the preparation of the β -esters it is necessary to apply the alkyl iodide or the alkyl sulphate, preferably the latter, to an alkaline solution of the corresponding acid. The following methyl esters were prepared: *Methyl glyoxylate phenylhydrazine*, α -form, needles or leaflets, m. p. 137° (compare Harries, A., 1903, i, 605); β -form, yellow crystals, m. p. near 70°. *Methyl glyoxylate m*-4-xylylhydrazine, α -form, silky needles, m. p. 142—143°; β -form, pale yellow needles, m. p. 69°. *Methyl glyoxylate ψ -5-cumylhydrazine*, α -form, yellow needles, m. p. 175°; β -form, yellow needles, m. p. 86°. *Methyl glyoxylate p*-bromophenylhydrazine, α -form, needles, m. p. 191—192°; β -form, leaflets, m. p. 102°. *Methyl glyoxylate phenylmethylhydrazine*, only one form obtained, yellow platelets, m. p. 61—62° (see above).

The esters are more stable than their parent acids. When heated to fusion the α -esters undergo partial transformation into their β -isomerides, a similar equilibrium generally being attained if either modification is kept with methyl-alcoholic sulphuric acid at the ordinary temperature. Concentrated alcoholic hydrogen chloride causes intermolecular condensation, the α -form of methyl glyoxylate phenylhydrazine being converted into *ethyl glyoxylate phenylazoacetylphenylhydrazine*,



orange-red needles, m. p. 154° , with concurrent displacement of the methyl group by ethyl; the corresponding *acid*, $C_{16}H_{14}O_3N_4$, forms orange-coloured needles, m. p. 225° (decomp.). By the action of acetic anhydride and sodium acetate aided by heat, both the α - and β -forms of an ester are converted into the acetyl derivative of the α -isomeride, the phenylhydrazone of methyl glyoxylate yielding an *acetyl* derivative, $C_{11}H_{12}O_3N_2$, colourless needles, m. p. 105° , whilst the stereoisomeric *m*-4-xylylhydrazones give an *acetyl* compound, $C_{13}H_{16}O_3N_2$, colourless needles or prisms, m. p. 88° .

Nitrous acid reacts with the α - and β -forms of glyoxylic acid phenylhydrazone producing benzeneazoformaldoxime (compare Busch and Meussdörffer, *loc. cit.*), whilst with the corresponding esters only the α -isomerides are affected, the product being the expected alkyl arylazoformaldoximecarboxylate; thus the phenylhydrazone of methyl glyoxylate yields *methyl phenylazoformaldoximecarboxylate*, $NPh \cdot N \cdot C(:NOH) \cdot CO_2Me$, red crystals, m. p. 136° , whilst the *m*-4-xylylhydrazone and ψ -5-cumylhydrazone compounds respectively give rise to red crystals, m. p. 152° , and red needles, m. p. 170° , presumably of the corresponding *oxime* derivatives. Glyoxylic acid phenylmethylhydrazone and its methyl ester are inert towards nitrous acid, but pyruvic acid phenylhydrazone gives phenylazoacetaldoxime with loss of carbon dioxide. The marked difference in behaviour between the α - and β -isomerides of the arylhydrazones of glyoxylic acid discords with the view of their stereoisomeric nature, and is to be examined further.

It was hoped by the action of phenylcarbimide on the isomeric hydrazones to obtain isomeric semicarbazones, of which the relative structure could be clearly distinguished by their chemical properties, especially the ease of ring formation. Unfortunately, however, the arylhydrazones of glyoxylic acid refused to react with phenylcarbimide, and with the methyl esters a definite result was obtained only with the phenylhydrazone compound; in this case the necessary temperature was so high that partial isomerisation occurred; but as the β -isomeride appeared to be unaffected by phenylcarbimide, the resulting *methyl glyoxylate diphenylsemicarbazone*, $CO_2Me \cdot CH:N \cdot NPh \cdot CO \cdot NPh$, colourless needles, m. p. 159° , is probably derived from the α -form of the parent ester; the corresponding *glyoxylic acid diphenylsemicarbazone*, $C_{15}H_{13}O_3N_3$, forms colourless needles, m. p. 191° . These products exhibited no tendency to ring formation, either alone or on oxidation, and so furnish slight confirmatory evidence of the structure assumed for the α -isomerides.

In an endeavour to obtain the hydrazones of the anilide of glyoxylic acid, dichloroacetanilide and phenylhydrazine were caused to react in boiling alcoholic solution containing pyridine; the product, however, was phenylazoformaldehyde phenylhydrazone, $NPh:N \cdot CH:N \cdot NPh$, probably formed by concurrent oxidation and condensation of phenylhydrazine and the phenylhydrazone of glyoxylic anilide or acid.

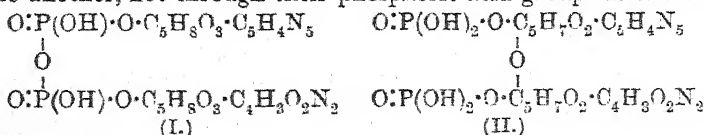
D. F. T.

Specific Gravity of Aqueous Solutions of Hens' Egg-albumin. M. A. RAKUZIN and G. D. FLIER (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 458—461).—The albumin of hens' eggs represents a saturated solution containing about 15% of the albumin, together with small proportions of fat and salts. At 17°, the saturated solution contains 15.35%. The values of D_{17}^{17} for solutions of different concentrations are: 1%, 1.00283; 5%, 1.01341; 10%, 1.02666; 15%, 1.03942. The limiting solubility of albumin being 15.35%, the specific gravities for solutions of higher concentrations (up to 60%) given in Witz's table (*Chemiker-Kalendar*) are without experimental foundation. For 5% solutions, the following results were obtained: (1) untreated egg-albumin, D_{15}^{15} 1.01341, $[\alpha]_D - 36.6^\circ$; (2) fat-free albumin, prepared by extraction with light petroleum, D_{15}^{15} 1.01314, $[\alpha]_D - 36.6^\circ$; (3) fat- and salt-free albumin, obtained by treating a solution of the fat-free albumin with lead acetate and decomposing the lead albuminate with hydrogen sulphide, D_{15}^{15} 1.01288, $[\alpha]_D - 36.6^\circ$. T. H. P.

Legumin as the Analogue of Casein. M. A. RAKUZIN and (MLLE.) G. F. PEKARSKAJA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 469—470).—Legumin (Merck's) resembles casein in its physical and chemical characters. Contrary to the statement of Osborne and Harris concerning the legumin of horse-beans, it does not dissolve in 10% sodium chloride solution, but it dissolves in water containing 0.5% of hydrochloric acid (1:2) and 0.2% of pepsin, its specific rotation in this solution being $[\alpha]_D - 42.88^\circ$. It contains 0.16% of phosphorus, and it gives the following colour reactions, the sensitiveness being indicated in brackets: biuret (1:3030), Millon's (1:1510), Adamkiewicz's (1:14920), Molisch's (1:14920), Pettenkofer's (1:3030), and Ostromisslenski's (1:1510). T. H. P.

Adenine-uracil-dinucleotide and the Structure of Yeast-Nucleic Acid. WALTER JONES and B. E. READ (*J. Biol. Chem.*, 1917, **29**, 111—122).—*Adenine-uracil-dinucleotide* is obtained as an amorphous powder by the action of dilute ammonium hydroxide on yeast-nucleic acid. It is levorotatory, $[\alpha]_D - 6.8^\circ$, and gives a crystalline *tetrabrucine* salt, $C_{19}H_{25}O_{15}N_7P_2 \cdot 4C_{23}H_{26}O_4N_2 \cdot 14H_2O$, m. p. 174—175° (decomp.). On treatment of the dinucleotide with ammonia in an autoclave at 135°, adenosine is liberated, and is isolated as the picrate, m. p. 183.5° (corr.). Uridine is obtained from the filtrate by Levene and La Forge's method (*A.*, 1912, i, 325). The hydrolysis of the dinucleotide with sulphuric acid yields adenine and uracil.

The preparation of the above tetrabrucine salt of the dinucleotide indicates that the two mononucleotide groups are joined to one another, not through their phosphoric acid groups as ordinarily



represented (I), but through their carbohydrate groups (II). If (I) were correct, only a dibrucine salt could be obtained. It is probable that the same mode of nucleotide linking exists throughout the entire nucleic acid molecule (see next abstract).

H. W. B.

Mode of Nucleotide Linking in Yeast-Nucleic Acid. WALTER JONES and B. E. READ (*J. Biol. Chem.*, 1917, 29, 123—126. Compare preceding abstract).—When adenine-uracil-dinucleotide is heated with dilute sulphuric acid, half of its phosphoric acid is set free rapidly and completely, whilst the remainder is only slowly liberated. This indicates that one purine and one pyrimidine base are present in the molecule (compare Jones, A., 1916, ii, 356). Yeast-nucleic acid behaves in exactly the same way. Since it has been shown that the nucleotides in adenine-uracil-dinucleotide are combined through the carbohydrate groups (*loc. cit.*), it follows that the union of the four nucleotides in yeast-nucleic acid must also occur through the carbohydrate groups.

H. W. B.

Significance of the Condition of the Substrate in the Action of Pepsin. III. Pekelharing's Pepsin. W. E. RINGER (*Kolloid Zeitsch.*, 1916, 19, 253—276).—Little attention has hitherto been given to the condition of the colloidal substrate in enzyme reactions, but the experiments described in this paper show that this factor is of considerable importance. The observations have reference to proteolytic action under the influence of pepsin prepared according to Pekelharing's method. The fact that this pepsin is much more active than other pepsin preparations is considered to be due to its greater degree of purity.

According to cataphoretic experiments in an electrical field, this pepsin affords no evidence of the existence of an isoelectric point, the particles being under proteolytic conditions always negatively charged. When the anode and cathode liquids are separately examined, it is found that the anode portion is much more active as a proteolytic agent, but less rich in protein. This suggests that the pepsin represents a complex (possibly an adsorption compound) in which the enzyme proper is associated with a relatively large quantity of inactive protein.

In the investigation of the dependence of the proteolytic activity of the pepsin on the condition of the substrate, experiments were made with undissolved albumin in which the solvent capacity of the pepsin was determined; further, with dissolved albumin in which the first stage in the proteolytic action was examined, and also with hetero-, proto-, and deutero-albumoses in order to elicit information relative to later stages of the proteolytic series of changes.

The results obtained show that the two first-mentioned processes depend on the condition of the substrate, in that maximum activity of the enzyme corresponds with a maximum in the degree of hydration of the albumin as measured by the swelling of the substrate. According to the results for solutions of different acids, the

sequence of the acids, when arranged according to the activity of the pepsin, is the same as the sequence which gives the acids in the order of their swelling effects. The retarding influence of different salts on the proteolytic activity of the enzyme is also found to run parallel with the influence which these salts exhibit in reducing the swelling of the albumin in acid solution.

In the later stages of the proteolytic series, when the condition of the substrate is subject to relatively less variation, the activity of the pepsin would seem to be affected to a greater extent by other factors, of which the hydrogen-ion concentration is of particular importance. It has, of course, been supposed that this is the main factor in all enzyme reactions of this type, but the facts adduced by the author seem to show that the condition of the substrate is probably of greater importance when the reaction in question is such that considerable variations in the substrate are possible.

H. M. D.

A Comparative Study of the Proteolytic Enzymes—Erepsin from the Intestine and Ereptase from Yeast. K. G. DERNBY (*Medd. Nobel Inst.*, 1916, 3, (14), 1—30).—The conversion of glycylglycine into glycine under the influence of the enzyme erepsin obtained from the duodenum of the pig and of ereptase extracted from yeast press-juice has been examined in a series of experiments.

For both enzymes, the optimum hydrogen-ion concentration at 38° is approximately that corresponding with $p_H=7.8$. If the enzyme concentration relative to that of the dipeptide is sufficiently great, the transformation occurs in both cases in accordance with the equation for a unimolecular reaction. There is, however, a very marked difference between the two enzymes in respect of the effects which are produced by the addition of neutral salts. In the case of ereptase, the influence of added salts is very slight, whereas the rate of hydrolysis by erepsin is greatly reduced when salts are added to the solution. The retarding effect is independent of the nature of the ions, and appears to be determined solely by the total concentration.

Similar experiments on the proteolytic action of the enzymes with polypeptides have shown that the decomposition takes place much more slowly than in the case of glycylglycine. Towards peptone, the two enzymes behave very similarly, but casein is acted on more rapidly by erepsin than by ereptase.

On account of the sensitiveness of erepsin to the influence of neutral salts, ereptase is to be preferred to erepsin for experimental work in the kinetic investigation of proteolytic processes.

H. M. D.

Physiological Chemistry.

The Permeability of Red Blood Corpuscles to Electrolytes.

H. ROHONYI (*Koll. Chem. Beihefte*, 1916, **8**, 337—376).—The permeability of red blood corpuscles to electrolytes has been examined in experiments with aqueous solutions of nitrites, chlorates, and ferricyanides, under the influence of which the hæmoglobin is transformed into methæmoglobin. When the blood corpuscles are subjected to the action of solutions of the nitrites, the nitrite ion is absorbed, and this absorption is accompanied by the removal of the chlorine ion from the corpuscles. The chlorine ion re-enters the corpuscles when these are subsequently exposed to the action of a sodium chloride solution. The ionic transfer is independent of the relative magnitudes of the osmotic pressures of the inside and outside solutions. The absorption of the nitrite ion is accelerated by cations and retarded by anions. The retarding influence of the anions decreases in the order: thiocyanate, oxalate, nitrate, iodide and chloride, sulphate. The sequence is independent of the hydrogen-ion concentration of the solutions, but if the solutions are very dilute, the anions increase the rate of absorption of the nitrite ion.

The absorption effects observed with hæmolyzed blood and with a solution of crystallised hæmoglobin are almost identical with those found in the experiments with blood corpuscles. This identity was also found in the absorption of the chlorate ion, which only occurs at higher temperatures. On the other hand, the ferricyanide ion in neutral solution is absorbed by hæmolyzed blood, but not by the corpuscles. In acid solution, ferricyanides cause agglutination, which process takes place previously to the transformation of the hæmoglobin.

From the above observations, the author concludes that blood corpuscles have no specific covering membrane, and that the absorption of ions by hæmoglobin is a process which is fundamentally identical with the absorption of ions by suspended particles and by colloids.

H. M. D.

The Action of Carbon Dioxide and Oxygen on the Permeability of Red Blood Corpuscles to Electrolytes.

H. ROHONYI and A. LÓRÁNT (*Koll. Chem. Beihefte*, 1916, **8**, 377—390).—Under the influence of carbon dioxide, there is a transference of chloride from the serum to the red blood corpuscles, and at the same time the alkalinity of the serum increases. These changes in the distribution of chloride and alkali between corpuscles and serum are also found when the structure of the corpuscles is destroyed by hæmolysis. It is suggested that the proteins of the red corpuscles under the influence of carbon dioxide react with the sodium chloride, absorbing the chlorine ion and producing sodium carbonate, the presence of which in the serum increases the alkalinity.

A new method for the estimation of the alkali titre of serum and albuminous liquids is described. This method depends on the fact that the proteins are coagulated by potassium ferricyanide when, by addition of acid, the hydron concentration is raised to a value which differs only slightly from the neutral point. The titration is made with $N/20$ sulphuric acid, and special experiments have shown that the end-point is not affected by the presence of carbonic acid.

H. M. D.

Two Peculiarities of Red Blood Corpuscles (Endocoagulation and Reversal of Hæmolysis). H. ROMONVI (*Koll. Chem. Beihefte*, 1916, 8, 391—398).—If a substance, which coagulates proteins, is added to a suspension of red blood corpuscles, coagulation of the hæmoglobin occurs within the corpuscle. The conditions under which this endocoagulation takes place are nearly the same as those which obtain in the coagulation of hæmolysed blood and of a solution of crystallised hæmoglobin.

The reversal of hæmolysis has been observed on the addition of protein-coagulating substances to a hæmolysed blood solution. This phenomenon and the facts relating to endocoagulation are considered to afford evidence against the view that red blood corpuscles have a covering membrane, the selective permeability of which is supposed to play a considerable part in determining the characteristic properties of the corpuscles.

H. M. D.

Cholesterol and Cholesterol Esters in Human Blood. W. R. BLOOR and ARTHUR KNUDSON (*J. Biol. Chem.*, 1917, 29, 7—13. Compare A., 1916, ii, 650).—A constant relation exists between free cholesterol and cholesterol esters in normal and in most specimens of pathological blood, slight variations occurring only in cases of cancer and nephritis.

H. W. B.

Cholesterol in Human Blood under Pathological Conditions. W. DENIS (*J. Biol. Chem.*, 1917, 29, 93—110).—Estimations have been made of cholesterol in the blood of normal individuals and of a large number of persons suffering from the more common diseases, including nephritis, syphilis, diabetes, typhoid fever, pneumonia, pleurisy, cancer, etc. A slight increase in cholesterol content was noted only in a few of the cases of diabetes. Low cholesterol values do not appear to be characteristic of any special pathological condition other than marked prostration. The author draws the conclusion that cholesterol estimations in blood do not have, at present, any value for clinical diagnosis or prognosis.

H. W. B.

Hæmocyanin. CH. DHÉRE (*J. Physiol. Pathol. gén.*, 1916, 16, 985—997. Compare A., 1905, i, 164; 1910, i, 647).—For the estimation of copper in the blood of molluscs and crustacea (present in the respiratory pigment hæmocyanin) the organic matter is destroyed by heating with sulphuric and nitric acids, the copper is

deposited electrolytically on platinum, is dissolved off by nitric acid, and estimated colorimetrically as ferrocyanide. The blood of *Octopus* and of *Sepia* is richest in copper, on the average 23.5 mg. of Cu in 100 c.c. of blood. That of *Homarus vulgaris* contains 10 mg., of *Helix pomatia*, 6.5—7.5 mg. per 100 c.c. A bibliography of forty-six papers is given. G. B.

Feeding Experiments with Deficiencies in the Amino-acid Supply. Arginine and Histidine as possible Precursors of Purines. HAROLD ACKROYD and FREDERICK GOWLAND HOPKINS (*Biochem. J.*, 1916, 10, 551—576).—When arginine and histidine are together removed from the diet of rats which have been previously growing on a complete amino-acid mixture, there is a rapid loss of body-weight and a decrease in the amount of allantoin excreted in the urine. When the amino-acids are replaced, growth recommences, and the excretion of allantoin returns to the normal. When only one of these acids is withdrawn, loss in body-weight is not observed, and there may even be growth; the fall in urinary allantoin is also slight. Nutritional equilibrium is possible, therefore, in the absence of one of these related amino-acids, but not in the absence of both. The authors suggest that this is because each one of them can, in metabolism, be converted into the other.

The removal of tryptophan from the food produces a nutritional failure, which is even greater than when arginine and histidine are withheld. The absence of vitamins also results in a rapid loss in body-weight. In neither of these cases, however, is there any diminution in the excretion of urinary allantoin. Since allantoin is the end-product of purine metabolism in these animals, the authors consider that arginine and histidine play a special part in purine metabolism, probably constituting, in fact, the raw material (or the most readily available raw material) for the synthesis of the purine ring in the animal body. H. W. B.

Relative Value of Certain Proteins and Protein Concentrates as Supplements to Corn Gluten. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL, with EDNA L. FERRY and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1917, 29, 69—92).—The authors present data regarding the growth of rats and showing the relative nutritive values of a number of proteins and protein "concentrates" when used to supplement corn gluten in an otherwise adequate ration. The products studied include caseinogen, lactalbumin, edestin, cottonseed protein, soja bean flour, beef, brewer's grains, pea meal, peanut meal, etc. These food materials vary greatly in their efficiency for promoting growth when employed in conjunction with corn gluten; and this variability is dependent primarily on the relative content of lysine and tryptophan. Corn gluten is deficient in these amino-acids, and their addition as such, or in the form of proteins yielding them, renders the corn gluten suitable for promoting growth.

Of the various proteins employed to supplement the inefficient corn gluten, lactalbumin is by far the most effective. Brewers'

grains and distillers' grains are the least effective, presumably on account of their low content of lysine. Evidence is afforded that the small additions of the more efficient proteins actually supplement the corn gluten instead of themselves furnishing all the protein used for growth, in that equivalent amounts of these proteins alone in a similar ration are incapable of inducing a comparable degree of growth. Small amounts of a superior protein are often just as efficient for growth as larger amounts of a less adequate protein. Attention is directed to the probable value of these results in practical animal husbandry. H. W. B.

Growth of Rats on Diets of Isolated Food Substances.

THOMAS BURR OSBORNE and LAFAYETTE BENEDICT MENDEL (*Biochem. J.*, 1916, 10, 534—538).—The authors are in agreement with Drummond (*A.*, 1916, i, 522) that both fat-soluble and water-soluble accessory substances are necessary for growth. H. W. B.

Non-existence of Free or Combined Lecithin in Egg-yolk and in Animal and Vegetable Biological Structures. NICOLA ALBERTO BARBIERI (*Gazzetta*, 1917, 47, i, 1—37).—The fatty substances of egg-yolk may be completely removed in a pure condition by means of neutral solvents, and on hydrolysis they yield only glycerol and aliphatic acids. These fatty substances may hold, in a state of solution or suspension, nitrogenous or chromatin principles and phosphates which may be removed by either dialysis or hydrolysis with a very dilute acid, or repeated washing with distilled water in presence of alcohol, without the formation of any trace of glycerol from the fatty substances. The whole of the phosphorus of egg-yolk occurs in the form of phosphoric acid combined with potassium, sodium, calcium, and magnesium. In no case can glycerophosphoric acid be obtained by treating the egg-yolk with a neutral solvent, as this compound makes its appearance only after hydrolysis; if the alkali soap is decomposed by means of acid, the glycerol passes into solution, together with the phosphoric acid derived from the phosphates. The conclusion is drawn that the glycerol of the supposed lecithin actually exists in egg-yolk combined with aliphatic acids to form fats. Further, egg-yolk contains no trace of choline, the supposed biological choline being a product either of the degradation of ovochromin or of putrefaction.

T. H. P.

Distribution of Esterases in the Animal Body.

AGNES ELLEN PORTER (*Biochem. J.*, 1916, 10, 523—533).—Enzymes capable of hydrolysing fats and waxes are widely distributed among the organs of man, ox, sheep, pig, cat, rabbit, and guinea-pig. Butyrylase and lecithase are always present, whilst lipases for splitting olein, stearin, and palmitin occur in most organs, particularly in the pancreas and liver. Wax-splitting enzymes are found in several parts of the body besides the skin.

The author directs attention to the fact that those animals which, like the guinea-pig, are very susceptible to tubercle, are compara-

tively poor in esterases, whilst animals, such as the cat, which are seldom attacked by this disease are well provided with them. In all species the lungs are comparatively deficient in esterases.

H. W. B.

Chemical Examination of the Oil from the Australian Dugong. R. W. CHALLINOR and A. R. PENFOLD (*J. Soc. Chem. Ind.*, 1917, **36**, 192—195).—The specimen of oil investigated was obtained from the blubber of a single animal. It was of a pale straw tint, clear and limpid, and without pronounced taste. On keeping, a copious, white, crystalline deposit, consisting of innumerable wheatsheaf-like bundles of needles, separated, which was completely redissolved at 33° and remained in solution for some hours, even when the temperature had fallen below 20°. It had $D_{15.5}^{20}$ 0.9161, n_D^{20} 1.4628, $\alpha_D -0.21$ (in a 2-dm. tube), iodine number 84.26, acid number 0.31, free acid as oleic acid 0.15%, saponification number 200.3, unsaponifiable matter 0.61%. The mixed fatty acids had n_D^{40} 1.4499, D_{15}^{20} 0.8811, D_{30}^{20} 0.8867, m. p. 35—36°, solidifying point 33°, iodine number 66.19, neutralisation number 180.4, mean mol. wt. 310.43, and yielded 0.77% of polybromide insoluble in ether. (The latter forms a white powder, which turns slightly grey on drying at 100°; it darkens a little at 200° and decomposes at 220°.) The acids were separated into solid and liquid portions by the modified Gusserow-Varrentrapp process, the percentage of liquid acids being 65 (iodine number 94.45) and of solid acids 25 (iodine number 4.72). The latter had n_D^{60} 1.4390, D_{15}^{60} 0.8911, D_{30}^{60} 0.8782, m. p. 51°, iodine number 4.63, neutralisation number 207.49, mean mol. wt. 269.89. The physical constants of the former were n_D^{30} 1.4567, $\alpha_D^{25} -0.18^\circ$, D_{15}^{25} 0.8999, iodine number 29.58, neutralisation number 202.37, mean mol. wt. 276.7.

The slight levorotation of the oil suggests that the unsaponifiable matter is probably cholesterol, more especially as the latter, if present, would find its way into the liquid acids by the usual methods of separation and render them optically active also, which is in accordance with the author's observations. The constants found for the liquid acids indicate that oleic acid is the principal constituent, together with a small amount of a highly unsaturated acid. Further details are promised in a subsequent communication.

H. W.

Action of the Alkaline-earth Chlorides on Urinary Acidity. CHARLES MAYER (*Bull. Soc. chim.*, 1917, [iv], **21**, 19—25).—The ingestion of magnesium chloride, to an extent insufficient to produce colic, causes a marked rise in the acidity-coefficient of the urine, as calculated from the formula $100n/2000(D-1)$, where n is the volume of standard alkali hydroxide required to neutralise the urine, phenolphthalein being the indicator, and D is the density of the urine. This rise in acidity is only accompanied by a very small diminution in the phosphoric acid content of the urine, the two effects being by no means comparable. The author considers that de Jager's explanation as to the rise in acidity (compare A.,

1912, ii, 276) is insufficient, and that the increase is also due to the interaction, in the intestine, of the magnesium chloride with sodium salts of the fatty acids giving insoluble magnesium salts of these acids and sodium chloride. Normally, the sodium salts would be converted into sodium hydrogen carbonate, which would tend to keep the urinary acidity down. W. G.

Excretion of Creatine and Creatinine Parenterally Introduced. J. F. LYMAN and J. C. TRIMBY (*J. Biol. Chem.*, 1917, 29, 1—5).—Subcutaneous injections of creatine into rabbits and man are followed by increased urinary excretion of creatinine, indicating the occurrence of a transformation of creatine into creatinine in the body. In man, about 4% of the injected creatine is excreted unchanged and 20% transformed into creatinine; the fate of the remainder is not established.

The injection of creatinine does not lead to the excretion of creatine in the urine, but it is pointed out that this does not prove that the change in this direction does not occur. H. W. B.

Sugar Formation. I. Experiments with Glycine, Glycine Anhydride, Aminoethyl Alcohol and Glycolaldehyde. MAX CREMER and RUDOLF W. SEUFFERT, with BERGER, PAPE, and FABISCHE (*Beitr. Physiol.*, 1916, 1, 255—286; from *Chem. Zentr.*, 1916, ii, 1045).—An account is given of the experimental work of Berger, Pape, and Fabische on the formation of sugar in the phloridzin diabetic organism. Cremer's equation for the degradation of glycine, $4\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H} = \text{C}_6\text{H}_{12}\text{O}_6 + 2\text{CO}(\text{NH}_2)_2$, demands the conversion of one and a-half atoms of carbon for each nitrogen atom. This result was obtained in Berger's best experiments with a phloridzin diabetic dog. Pape's experiments confirm this conclusion, but the observed values are lower than the theoretical figures, from which it is inferred that the whole of the neoglucose does not necessarily appear as 'extra' sugar. Administration of glycine anhydride causes the appearance of considerably less 'extra' sugar than that of glycine. This confirms the results of other authors, and shows that a considerable portion of glycine anhydride escapes combustion within the organism or is not degraded beyond the glycine stage. Fabische's experiments were undertaken with the object of establishing the process by which aminoacetic acid is converted into dextrose (compare Schwenken, A., 1914, i, 1156). Aminoacetaldehyde and aminoethyl alcohol, as reduction products, are closely related to glycine. Administration of aminoethyl alcohol to phloridzinised animals caused distinct narcosis and gave variable results for 'extra' sugar, so that a definite conclusion could not be drawn. Subcutaneous injection of glycolaldehyde gave signs of sugar formation, but the animal became ill on the third day. H. W.

Flavine and Brilliant-Green. Powerful Antiseptics with Low Toxicity to the Tissues. C. H. BROWNING, R. GULBRANSEN, E. L. KENNAWAY, and L. H. D. THORNTON (*Brit. Med. J.*, 1917, i, 73—76).—Most antiseptics examined so far act much more

powerfully in water than in blood serum (compare, for example, Bechhold and Ehrlich, A., 1906, ii, 383), but it has now been found that the reverse holds for 2:8-diamino-10-methylacridinium chloride, a substance originally prepared by Benda (A., 1912, i, 651), at Ehrlich's suggestion, as a trypanocide, and known as trypaflavine. This substance, "flavine," kills *Staphylococcus aureus* at 1:20,000 in water containing 0.7% peptone, but at 1:200,000 in blood serum. For *Bacillus coli*, the corresponding dilutions are 1:1300 and 1:100,000. A 0.1% solution has been used clinically with success, and, as regards staphylococci, it is equivalent to 80% phenol. Flavine has a very low toxicity; 300 c.c. of a 1:1000 solution has been given to man intravenously, and phagocytosis is only inhibited by 1:500 solutions. A tabular comparison with other antiseptics is given. G. B.

Radium as a Substitute, to an Equiradio-active Amount, for Potassium in the so-called Physiological Fluids. H. ZWAARDEMAKER and T. P. FEENSTRA (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, 19, 633—636).—It has been found that the potassium in a Ringer's solution may be replaced by radium without any alteration in the effect which the solution has on the beating of a frog's heart if the quantity of radium is such that its total radio-activity is the same as that of the potassium. In combination with previous observations, these experiments show that the potassium of the normal Ringer's solution may be replaced by rubidium, uranium, thorium, and radium without altering its influence on the cardiac pulsations if the quantities of the several metals are equivalent in radio-active power. H. M. D.

The Salicylates. IV. Salicylate in the Blood and Joint Fluid of Individuals receiving Full Therapeutic Doses of the Drug. R. W. SCOTT, T. W. THOBURN, and P. J. HANZLIK (*J. Pharm. Expt. Ther.*, 1917, 9, 217—225).—The concentration of salicylate in the blood and joint fluids of rheumatic individuals receiving full therapeutic doses of the drug is approximately the same, namely, 0.02%. The authors were unable to detect free salicylic acid in the joint fluid of individuals suffering with rheumatic fever. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Disinfecting Power of Complex Organic Mercury Compounds. III. Mercuriated Phenols. (WALTHER SCHRAUTH and WALTER SCHOELLER (*Zeitsch. Hyg. Infektkrankh.*, 1916, 82, 279—288; from *Chem. Zentr.*, 1916, ii, 1054).—The results previously obtained by the authors with the substitution products

of sodium *o*-hydroxymercuribenzoate, $\text{HO}\cdot\text{Hg}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Na}$ (A. 1912, ii, 376), lead to the conclusion that the disinfecting power would be increased by the substitution of the less acidic phenolic hydroxyl for the carboxyl group. Experiments have now been performed with two mercuriated phenols, and also with substances which contain, in addition to one or two hydroxymercuri-groups, halogen, alkyl, or methoxy-groups. The previous observations have been confirmed in all cases, and the influence of the position of the substituent in the benzene nucleus has been investigated. It has been further observed that the relative positions of the hydroxymercuri- and phenolic groups are important. Considerable differences in the disinfecting power of the three isomeric mercuriated cresols have been noticed; the *m*-derivative is most potent, whilst sodium *o*-hydroxymercuriphenoxide is more active than the isomeric para-compound. In the case of sodium dihydroxymercuriphenoxide (providol), it is shown that the entrance of a second hydroxymercuri-group into the benzene nucleus considerably increases the disinfecting power. The substances were prepared by treating the phenol with mercuric acetate in alcoholic solution; the recrystallised products were dissolved in the calculated amount of sodium hydroxide and diluted with water to the required mercury content. Among the preparations examined, sodium *o*-chlorohydroxymercuriphenoxide and sodium dihydroxymercuriphenoxide have been found particularly active. Their practical importance is increased by the fact that their disinfecting power, in contrast to that of all previously investigated compounds, is not diminished in the presence of soap, and that they are permanently unchanged in soaps which consist chiefly of the sodium salts of saturated fatty acids. Medical preparations of this kind (apidol- and providol-soap) keep well.

H. W.

Effect of Phosphorus on Lucerne and Lucerne Bacteria.

H. W. TRUESDELL (*Soil Sci.*, 1917, 3, 77—98).—Pure cultures of *Bacillus radiculicola* from lucerne were inoculated into sterilised soil to which phosphates had been added in the form of di-potassium, di-sodium, and di-calcium phosphates. Bacterial counts were made after seven and fourteen days, and in every case the numbers were larger where phosphate had been present than in the control cultures, the maximum increase in each case being 600% with di-potassium, 100% with di-sodium, and 15% with di-calcium phosphate.

At the same time lucerne was grown in pot cultures. Unsterilised soil was used, both uninoculated and inoculated with *B. radiculicola*, and with and without di-calcium phosphate. The phosphate appeared to stimulate the plants, especially during the seedling stage; it also encouraged nodule formation and increased the dry weight and nitrogen content of the plant. The author is of opinion that the phosphorus acts by a direct stimulation of the living cells, and more especially of those of the nodule bacteria.

L. M. U.

Influence of Salts on the Bacterial Activities of the Soil.

J. E. GREAVES (*Soil Sci.*, 1916, 2, 443—480).—A series of ammonification tests was carried out with soil containing 2% of dried blood, to which were also added the following salts: chlorides, nitrates, sulphates, and carbonates of sodium, potassium, calcium, magnesium, manganese, and iron. The salts were all added in fractions of their molecular weights, varying from 156×10^{-7} to 10×10^{-3} per 100 parts of soil, so that the results were strictly comparable. With nearly all the salts, some stimulation was obtained at the low concentrations, but beyond a certain point, increasing amounts of the salts gradually inhibited ammonification. The only salts which had an inhibitive effect in all concentrations were calcium chloride and nitrate, potassium chloride and sulphate, sodium sulphate and magnesium nitrate; calcium and magnesium carbonates, on the other hand, never produced any but stimulating effects, even in the highest concentrations. In a general way, it may be said that the acid radicle, rather than the metal, played the more important part in controlling the rate of ammonification, and that the order of decreasing toxicity amongst the salts was usually: chlorides, nitrates, sulphates, carbonates.

The results are also considered in relation to those obtained by Harris (A., 1915, i, 1091) on the effect of salts on the germination and growth of plants. Very similar quantities of the various salts are required to reduce plant growth to half its normal amount or to reduce ammonification by 50%. The author considers the increased osmotic pressure exerted by added salts to be an important factor in retarding bacterial activity in the soil, but he states that it is not the only one.

L. M. U.

Biological Changes in Soil during Storage. F. E. ALLISON (*Soil Sci.*, 1917, 3, 37—62).—A bacteriological study of soil samples was made immediately they were brought into the laboratory and after intervals of storage varying from two hours to eighteen or even sixty days. During the winter months the number of bacteria was much affected by the warmer temperature of the laboratory. In the first twenty-four hours the numbers fell, then rose to a maximum, after which a decline set in until the fourth day, followed by a very gradual rise, which was still apparent when the experiment was stopped on the eighteenth day. During the first day an interval of two hours might cause a change in numbers amounting to 30—40%. In the summer months the change in the numbers during the first few hours of storage was much less marked, and the subsequent decrease was considerably slower. Ammonification, nitrification, and nitrogen fixation were also determined, and fungi were counted in the summer tests. Ammonification varied very much, as did the bacterial numbers.

L. M. U.

Ammonifiability versus Nitrifiability as a Test for the Relative Availability of Nitrogenous Fertilisers. C. B. LIPMAN and P. S. BURGESS (*Soil Sci.*, 1917, 3, 63—75).—Nitrification and ammonification tests were carried out on the following

nitrogenous manures: dried blood, high grade tankage, steamed bone meal, cottonseed meal, and fish guano. For the ammonification tests each manure was mixed with each one of twenty-three selected soils at the rate of 2% of the soil, and incubated for seven days. For the nitrification tests each manure was mixed with each soil at the rate of 1% of the soil and incubated for four weeks. At the end of the incubation period ammonia and nitrates were determined.

The availability of the nitrogen as measured by these two methods gave absolutely different and frequently opposite results. Given the fact that plants usually prefer nitrates to ammonia as a source of nitrogen, the authors consider nitrification rather than ammonification to be the more trustworthy test of the availability of nitrogen in a manure.

L. M. U.

Nature of Nitrification and Ammonification. K. MIYAKE (*Soil Sci.*, 1916, 2, 480—492).—It is found that in experiments on ammonification and nitrification, if the rates of increase of ammonia and nitrate are plotted in a curve, the curve is very similar to that of autocatalytic chemical reactions in which one of the products of reaction accelerates the reaction. The maximum increase of ammonia and nitrate per unit time occurs when the total production is half complete, and the processes take place according to the formula $\log x/(A-x) = K(t-t_1)$, where x is the amount of ammonia and nitrate which has been produced at time t , A is the total amount of ammonia and nitrate produced during the process, K is a constant, and t_1 is the time at which half of the total amount of ammonia and nitric acid is produced. L. M. U.

Colouring Matter of Red Torulæ. ALFRED CHASTON CHAPMAN (*Biochem. J.*, 1916, 10, 548—550).—The absorption spectrum of the colouring matter extracted by chloroform or carbon disulphide from red torulæ differs considerably from that of carotene. The colouring matter of the torula consists, therefore, of some other substance than carotene or of a mixture of carotene with some other colouring matter.

H. W. B.

Influence of Certain Organic Substances on the Development of Plants. I. G. CIAMICIAN and C. RAVENNA (*Atti R. Accad. Lincei*, 1917, [v], 26, i, 3—7).—In view of the fact that the accessory substances of vegetable organisms, such as glucosides, alkaloids, colouring matters other than chlorophyll, etc., are regarded by some authorities as reserve food materials and by others as excretory products, the authors, who favour the former view, have investigated the influence of certain of these substances on the development of plants.

When an organic compound is introduced into an adult plant either by way of the roots or by inoculation into the stem, no apparent external change is produced, provided that the nature and amount of the substance are such that the plant remains alive.

The germination of beans and maize on cotton-wool is almost completely inhibited by watering with 0.1% mandelonitrile solution, whereas when an amygdalin solution of corresponding concentration (0.55%) is used, all the seeds germinate like those treated with water. If, however, the mandelonitrile is first administered some days after germination, the plants develop, although comparatively slowly, the height attained being less and the root-growth not so marked; on the other hand, the stems are thicker and the plants more robust, since they are able to live through the winter, whilst those provided with complete nutriment dry up in October. That these plants treated with mandelonitrile are nourished at the expense of the nitrogen of this compound whilst the benzaldehyde undergoes oxidation or other transformation, is shown by the absence of hydrocyanic acid or benzaldehyde, even after the extract of the plant has been treated with emulsin.

Hydrocyanic acid in 0.1% concentration retards or prevents the germination of beans and maize, and those plants (about 30%) which grow very soon die. Nicotine tartrate solution containing 0.1% of the alkaloid behaves similarly towards the seeds, and even when it is first applied subsequently to the germination, the plants grow slowly and abnormally. Strychnine tartrate of similar concentration has no apparent influence on the germination of the seeds, but the plants dry up after a few days. The action of caffeine or morphine is similar to that of strychnine. T. H. P.

Pectic Substances of Plants. SAMUEL BARNETT SCHRYVER and DOROTHY HAYNES (*Biochem. J.*, 1916, **10**, 539—547).—The authors describe a method for the preparation of the pectic substances of plants, in which the essential operation is the extraction of the residue, obtained after the expression of the juice, with a warm 0.5% ammonium oxalate solution. A substance of acidic character is thereby obtained from turnips, strawberries, rhubarb, and apples, which is soluble in water and is designated *pectinogen*. On keeping in alkaline solution at the ordinary temperature, pectinogen undergoes conversion into *pectin*, $C_{17}H_{24}O_{16}$, which is also of acidic character and is precipitated from its alkaline solution by acids as a gel insoluble in water.

An aqueous solution of pectinogen does not yield a precipitate when treated with a dilute solution of a calcium salt. Pectin, on the contrary, when dissolved in alkali and then neutralised, gives a gelatinous precipitate with calcium chloride. Addition of strong sodium hydroxide to pectin solutions also yields a gelatinous precipitate.

On distillation with hydrochloric acid, pectinogen yields furfuraldehyde in such a quantity as to indicate that one pentose group is contained in each molecule of pectinogen. H. W. B.

Estimation of Hydrocyanic Acid and the Probable Form in which it Occurs in Sorghum vulgare. J. J. WILLAMAN (*J. Biol. Chem.*, 1917, **29**, 25—36).—In most cases, distillation of sorghum leaves with 5% tartaric acid yields less hydrocyanic acid

than is obtained when the macerated leaves are first allowed to undergo autolysis and are then subjected to the distillation process. In some cases the latter method of treatment yields hydrocyanic acid, whilst a similar sample treated by the first method, especially if it is ground with the tartaric acid solution before distillation, fails to indicate the presence of any acid. The author finds that amygdalin is not hydrolysed by 5% tartaric acid solution, and, relying on the resemblance between amygdalin and the glucoside, dhurrin, present in sorghum leaves, draws the conclusion that hydrocyanic acid is usually present in sorghum, not only in glucosidic combination, but also in another undetermined form.

Hydrolysis of the dhurrin in sorghum by the glucosidase present in the same tissues takes place very rapidly at 45°, but it is entirely prevented if the tissues are first macerated with 5% tartaric acid. Even in the presence of tartaric acid, retention of hydrocyanic acid by the tissues occurs during distillation, and this retention is not appreciably lessened by distilling under reduced pressure.

H. W. B.

Effect of Anæsthetics and of Frosting on the Cyanogenetic Compounds of Sorghum vulgare. J. J. WILLAMAN (*J. Biol. Chem.*, 1917, 29, 37—45. Compare preceding abstract).—Sorghum leaves exposed for a few days to the vapour of chloroform, ether, or alcohol, yield more hydrocyanic acid, both glucosidic and non-glucosidic, than the normal leaves. The author suggests that the anæsthetic stimulates both the hydrolytic and the synthetic actions of the cyanogenetic enzymes. An enzymic powder prepared from the chloroformed leaves is about twenty-five times as active towards amygdalin as a similar powder prepared from normal leaves.

Leaves subjected to a low temperature also contain more glucosidic and non-glucosidic hydrocyanic acid than ordinary leaves. Confirmation is thus furnished of the well-known statement that sorghum is especially poisonous after a frost.

H. W. B.

Physical Chemistry of Foods. II. Reduction of the Acidity of Wine with Calcium Carbonate (Chaptalising). Tartaric Acid and its Salts. THEODOR PAUL (*Zeitsch. Elektrochem.*, 1915, 21, 542—559. Compare A., 1915, ii, 590).—With the object of placing the process of deacidifying wines by means of calcium carbonate on a scientific basis, the author has studied in great detail the physico-chemical properties of tartaric acid and its sodium, potassium, calcium, and barium salts. The investigation has led to the following results: Since the acidity of a wine is defined as its hydrogen-ion content, it follows that the deacidifying constitutes a reduction of the hydrogen-ion concentration. In this process, the chemical equilibrium between normal calcium tartrate and tartaric acid, as well as that between calcium carbonate and tartaric acid, is the controlling factor. The solubility of calcium tartrate in carbon dioxide-free distilled water at 18° is 0.3802 gram per litre, that is, 0.001462 gram-mol. per litre. In distilled water which contains the equilibrium quantity of carbon dioxide the solubility is greater, amounting to 0.4096 gram = 0.001575 gram-mol. per litre at 18°. The equivalent con-

ductivity of normal calcium tartrate and disodium and dipotassium tartrates has been measured down to $v=40,000$. The migration velocity of the secondary tartrate ion ($\frac{1}{2}\text{C}_4\text{H}_4\text{O}_6''$) has been calculated and found to be 55.6 at 18° . The depression of the solubility of calcium tartrate by calcium chloride and by potassium tartrate has been determined, and the degree of dissociation calculated, and values obtained which agree well with those obtained from the electrical conductivity measurements. The solubility product of normal calcium tartrate at 18° has the value 0.77×10^{-5} . The acidity of tartaric acid solutions (1–16 per 1000) was determined by the sucrose inversion method, and values obtained which agree well with those obtained from the conductivity measurements. An addition of 80 grams of ethyl alcohol per litre exercises a considerable influence on the various equilibria existing in the solutions of tartaric acid and calcium tartrate, and consequently the alcohol content of wines must be taken into account when deacidifying with calcium carbonate. During the deacidifying of aqueous solutions of tartaric acid by calcium carbonate, the acidity decreases more rapidly at first than later for equal additions of calcium carbonate. The content of titratable acid, on the contrary, decreases regularly and in proportion to the amount of carbonate added. The same results are obtained during the deacidifying of natural wines, although the decrease in acidity is not at first quite so marked as in the case of aqueous solutions of tartaric acid. This is due to the earlier precipitation of normal calcium tartrate, since, generally, the wine already contains some calcium tartrate, and the presence of alcohol diminishes its solubility, and, further, wine contains other weak acids. The deacidifying of wine by calcium carbonate is therefore not a simple neutralisation. The addition of calcium carbonate brings about a change in the constitution and a marked shifting of the equilibria.

J. F. S.

The Influence of Various Cations on the Rate of Absorption of Ammonium Ion by Soil. K. MIYAKE (*Soil Sci.*, 1916, 2, 583–588).—A study of the rate of absorption of the ammonium ion by a soil from an $N/10$ -solution of ammonium chloride alone or in the presence of $N/100$ -, $N/20$ -, or $N/10$ -solutions of either sodium, potassium, magnesium, calcium, or aluminium chlorides. The results show that the relation between the time of contact of the soil and the solution and the amount of ammonium ion absorbed can be expressed by the equation $x = Kt^m$ (compare Cameron and Bell, U.S.A. Dep. Agr. Bur. Soils Bull., 30). The rate of absorption of ammonia from ammonium chloride is decreased by the presence of other chlorides, the retardation varying with the chloride present, and increasing with the concentration of the chloride. The retarding effect of the salts used increases in the order $\text{Na} < \text{Mg} < \text{Ca} < \text{Al} < \text{K}$. The acceleration of the retardation with increasing concentration is positive in the case of sodium, magnesium, and calcium chlorides, and negative in the case of aluminium and potassium chlorides.

W. G.

Ferrification in Soils. P. E. BROWN and G. E. CORSON (*Soil Sci.*, 1916, 2, 549—573).—In the first part of the paper an account is given of various methods which were tried for estimating the amount of ferrous iron in soils. None of these were successful, the results showing that ferrous compounds are adsorbed by the soil, and that organic matter, if present in any appreciable quantity, will cause an oxidation as well as a reduction of the iron compounds. Determinations were then made of what the authors call the “ferrifying power” (power of oxidising ferrous compounds) of various soils, this being the difference in the iron rendered soluble in 100 c.c. of sterile water plus 0.1 gram of ferrous carbonate after inoculation with an infusion of the soil and with a sterile infusion of the soil respectively, and incubation for varying periods of time. The results obtained show that the ferrification or deferrification, whilst common to the soils studied, depends on several factors, such as organic content of the soil, cultivation, moisture, etc. No definite correlation with any of these factors was found, but the cultivated soil had the greatest ferrifying power. Experiments conducted with pure cultures of bacteria and moulds show that the common soil organisms and moulds, as well as the iron bacteria, are capable of oxidising ferrous iron. W. G.

The Organic Matter of the Soil. II. A Study of Carbon and Nitrogen in Seventeen Successive Extracts; with some Observations on the Nature of the Black Pigment of the Soil. ROSS AIKEN GORTNER (*Soil Sci.*, 1916, 2, 539—548).—A continuation of previous work (compare *ibid.*, 1916, 2, 395). A silt loam soil was extracted with 1% hydrochloric acid until the filtrate no longer contained calcium, and it was then extracted nine times consecutively with fresh quantities of 4% sodium hydroxide solution, and then six times with 0.15% sodium hydroxide solution, the soil residue being dried and analysed. The first six extractions with 4% sodium hydroxide removed relatively more nitrogen than carbon from the soil, but the next nine extractions (three with 4% and six with 0.15% sodium hydroxide) removed relatively more carbon than nitrogen. The C/N ratio of the soil residue was much higher than that of the original soil. The work confirms the earlier observation that the black soil pigment is not soluble in 4% sodium hydroxide solution. It is, however, soluble in the 0.15% solution, from which it is precipitated either by the addition of sufficient sodium hydroxide to bring the strength of the solution up to 4%, or by the addition of salts of the heavy metals, or by acidifying the solution. The pigment cannot be dialysed, and forms a stable ammonium compound soluble in water, which is obtained by evaporating its ammoniacal solution to dryness. Attempts to prepare the pigment in a pure state were unsuccessful, the two preparations made containing, respectively, 37.47% and 51.17% of ash. The composition of the first sample, calculated on an ash-free basis, was C 61.3%; H 4.3%; O 31.6%; N 2.8%. W. G.

Organic Chemistry.

Cuprous isobutylxanthates. RICARDO MONTEQUI DÍAZ DE PLAZA (*Anal. Fis. Quim.*, 1917, 15, 54—60).—Cuprous isobutylxanthate, prepared from cupric sulphate and potassium isobutylxanthate, has a canary-yellow colour. When heated, it is decomposed, with formation of cupric sulphide. Its yellow solution in chloroform becomes red on warming, but the original colour is restored as the temperature falls. Pyridine transforms the salt into the red modification, which then dissolves. It is unaffected by cold, dilute hydrochloric acid, and only slightly attacked by the hot acid.

When the cupric sulphate is first reduced to the cuprous salt by means of sodium hyposulphite, the red form of the xanthate is produced. It is amorphous, and insoluble in water. Its alcoholic solution changes to the yellow modification, the same transformation being effected by acetone, benzene, carbon disulphide, and chloroform, and by heat. Dilute acids have no action on it, but hot, concentrated hydrochloric acid transforms it into the yellow modification.

It is suggested that the yellow variety has the double formula $(C_5H_9OS_2)_2Cu_2$, and the red modification the simple formula $C_5H_9OS_2Cu$.
A. J. W.

The Effect of Heat and Oxidation on Linseed Oil. JOHN ALBERT NEWTON FRIEND (*T.*, 1917, 111, 162—167).—When linseed oil is "thickened" by heat without appreciable oxidation, an increase is generally observed in the density and viscosity, whilst the coefficient of expansion undergoes a slight decrease; these results are probably due to polymerisation (compare Morrell, A., 1915, i, 75), the molecular weight of the "thickened" oil in benzene being greater than that of the original oil. It is worthy of note that the apparent molecular weight in benzene increases on dilution both for the raw and the heated oil.

Examination of linseed oil at various stages of oxidation between the raw oil and solid linoxyn several months old shows that there is a steady increase in density, but that the volume and weight both attain a maximum, although not simultaneously. The increase in weight at any time is not equivalent to the oxygen absorbed, because volatile matter is lost during the oxidation.

D. F. T.

An Isomeride of Glycuronic Acid. M. L. SAUREZ (*Chem. Zeit.*, 1917, 41, 87).—An acid is obtained from lemon pulp which yields a soluble barium salt having the formula $Ba(C_6H_9O_7)_2$; this salt when heated with concentrated barium hydroxide solution forms an insoluble yellow salt. The solution gives many of the reactions of glycuronic acid, but no compound is formed with

p-bromophenylhydrazine; the acid radicle could not be converted into glycuronic anhydride. The new acid yields mucic acid on oxidation, and is evidently an isomeride of glycuronic acid.

W. P. S.

Crystallisation and Complementary Properties of the Galactobiose previously obtained by Biochemical Synthesis. EM. BOURQUELOT and A. AUBRY (*Compt. rend.*, 1917, 164, 443—445. Compare A., 1916, i, 596).—Galactobiose has now been obtained in a crystalline form, the viscous deposit obtained from its solution in methyl alcohol on the addition of anhydrous ether having spontaneously crystallised after five months. The sugar was obtained in little spherical masses, with a taste slightly sweeter than that of lactose. Dried at 110° for one hour, it had $[\alpha]_D^{16} + 53.05^\circ$ and showed mutarotation, the results indicating that the product crystallising from methyl alcohol was in the α -form. The reducing power of galactobiose is 53.6% that of galactose.

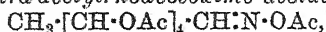
W. G.

Biochemical Synthesis, by means of Emulsin, of a Second Galactobiose. EM. BOURQUELOT and A. AUBRY (*Compt. rend.*, 1917, 164, 521—523).—From the residues from the preparation of the galactobiose previously described (compare A., 1916, i, 596; preceding abstract), by extraction with alcohol and subsequent recrystallisation from methyl alcohol, a second galactobiose has been obtained crystallising in microscopic needles, forming stellate clusters. After drying over sulphuric acid in a vacuum, it loses 13.63% of its weight at 110°, indicating the presence of 2MeOH of crystallisation. It softens at 147.5° (corr.) and has m. p. 180° (corr.). It shows mutarotation and has $[\alpha]_D + 35.01^\circ$, after drying at 110°. Its reducing power is 50.3% of that of galactose. It gives an *osazone*, yellow needles, m. p. 194°. It is hydrolysed in aqueous solution by sulphuric acid and by emulsin.

W. G.

Derivatives of Rhodeose (Degradation of Rhodeose). EMIL VOTOČEK (*Ber.*, 1917, 50, 35—41).—In the main, an account of the preparation of the oximes of rhodose and fucose, the acetylation of these, and the subsequent degradation to tetroses by Wohl's method.

Rhodeosoxime, $\text{OH}\cdot\text{CHMe}\cdot[\text{CH}\cdot\text{OH}]_3\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$, has m. p. 188—189°, $[\alpha]_D + 13.2^\circ$, and *fucosoxime* the same m. p. and $[\alpha]_D - 12.7^\circ$. *isoRhodose* does not react with hydroxylamine. The oximes are acetylated by adding them to a boiling mixture of acetic anhydride and sodium acetate, whereby *tetra-acetylrhodeosoxime*, $\text{CH}_3\cdot[\text{CH}\cdot\text{OAc}]_4\cdot\text{CN}$, and *tetra-acetylfucononitrile* are formed as very similar, crystalline substances, m. p. 177—178°. A small amount of *tetra-acetylrhodeosoxime acetate*,



m. p. 115—116°, is formed at the same time; this yields methyl-furfuraldehyde on distillation with hydrochloric acid (naphtha-resorcinol gives a brilliant magenta coloration with the vapours),

whereas the nitrile gives hydrogen cyanide salts on boiling with 20% potassium hydroxide or ammoniacal-alkaline silver nitrate. If the tetra-acetylrhodeonitrile is treated with ammoniacal silver oxide by Wohl's method, the diacetamide compound of rhodeotetrose, $C_6H_{15}O_5N_2$, m. p. 233° (decomp.), is formed. This may be hydrolysed to the rhodeotetrose, the *p*-bromophenylosazone of which crystallises in yellow, cell-like structures, m. p. $143-144^\circ$ (decomp.).

Rhodoose and fucose react with diphenylmethanedimethyldihydrazine (von Braun, A., 1910, i, 524), but *isorhodoose* does not. The *hydrazones*, $CH_2[C_6H_4 \cdot NMe \cdot N : CH(CH \cdot OH)_4 \cdot CH_3]_2$, are both pale yellow, crystalline powders which melt and decompose at 218° and 221° respectively. J. C. W.

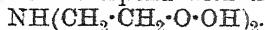
Behaviour of Sugars towards Diphenylmethanedimethyldihydrazine. J. VON BRAUN (*Ber.*, 1917, 50, 42-43).—The previous experience of aldehydic pentoses and hexoses, coupled with Votček's (preceding abstract), gives the author reason to suggest that diphenylmethanedimethyldihydrazine is a very useful agent for the determination of the configuration of the aldoses. Hydrazones are produced by ribose, lyxose, arabinose, rhamnose, rhodoose, fucose, mannose, and galactose, but not by xylose, *isorhodoose*, or dextrose, the feature common to the former class being that at least two of the three $\cdot CH \cdot OH$ groups following the aldehyde group have the same spatial arrangements. J. C. W.

Reaction between Starch and Formaldehyde, and the Supposed Diastatic Properties of Formaldehyde. WILHELM VON KAUFMANN (*Ber.*, 1917, 50, 198-202. Compare Woker, this vol., i, 61).—A severe criticism of the experiments on which Woker based her assumption that formaldehyde could imitate diastase in its hydrolysis of starch. The evidence was to the effect that in the presence of formaldehyde (the concentration was as much as 190 times that of the starch) starch soon lost its power of giving a blue colour with iodine. It is now stated that this is obviously due to the well-known fact that starch and formaldehyde combine (compare Syniewski, A., 1903, i, 68), for it is only necessary to remove the aldehyde by boiling, or to fix it by ammonia, or to hydrolyse the compound by adding an acid, to restore the starch completely. No fermentable sugar is formed and no change in rotation occurs. J. C. W.

Identity of the Synthetic Humin Substances with the Natural Humin Substances. L. C. MAILLARD (*Ann. Chim.*, 1917, [ix], 7, 113-152).—A theoretical paper in which the author, by a comparative study of the humin substances synthesised from reducing sugars and amino-acids (compare A., 1916, i, 597) and the natural humin substances, endeavours to establish their identity. W. G.

Explosive Peroxide Derivative of Hexamethylenetetramine. A. LEULIER (*J. Pharm. Chim.*, 1917, [vii], 15, 222-229).—When a mixture of 140 grams of hexamethylenetetramine, 140

grams of concentrated nitric acid, and 1220 grams of hydrogen peroxide is kept at 20° to 25° for four hours, a crystalline precipitate separates, which, when dry, is very explosive; it contains carbon 10%, hydrogen 10.06%, oxygen 45.50%, and nitrogen 10%, which composition would correspond with the formula

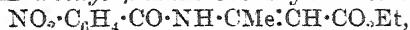


The substance is similar to the peroxide derivative prepared by Girsewald (A., 1912, i, 835), but differs in that it contains only 1 atom of nitrogen in its molecule.

W. P. S.

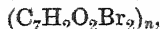
Acylation of Ethyl β -Aminocrotonate and Analogous Compounds. II. ERICH BENARY, FRITZ REITER, and HELENE SOENDEROP (*Ber.*, 1917, 50, 65—90. Compare A., 1909, i, 888).—In the earlier paper it was shown that ethyl β -aminocrotonate gives two *N*-acyl compounds when treated with either acetyl or benzoyl chloride, but that a derivative in which the acyl group is attached to carbon is formed in the case of chloroacetyl chloride. It would appear, therefore, that the strength of the acid has some influence on the reaction, and so the experiments have been extended to other acyl chlorides and to compounds analogous to ethyl β -aminocrotonate. The reaction is often difficult to explain, however, and no generalisations can yet be made. It is unsafe to predict whether the entering group will be attached to carbon or nitrogen, and at present it is necessary to prove the constitution of the product in each instance.

m-Nitrobenzoyl chloride reacts with the ester in the presence of pyridine to form α -ethyl β -*m*-nitrobenzoylaminoacronate,



in hexagonal prisms, *m. p.* 150°, which changes into the β -isomeride, glistening leaflets, *m. p.* 74°, when dissolved in acetyl chloride and then reprecipitated by pouring into ice-cold sodium carbonate. The corresponding ethyl β -*p*-nitrobenzoylaminoacronates are: α -, glistening leaflets, *m. p.* 145°; β -, needles, *m. p.* 126°. These yield the corresponding nitrobenzamides on boiling with dilute sulphuric acid, which proves the mode of attachment of the acyl group. *o*-Nitrobenzoyl chloride and *o*-bromobenzoyl chloride yield the benzamides at the outset, and *p*-bromobenzoyl chloride gives *p*-bromobenzoic anhydride.

o-Acetoxybenzoyl chloride gives no definite result, and 3:5-dibromosalicyl chloride only forms a dibromosalicylide,

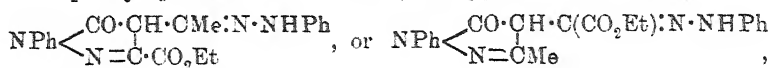


m. p. 316°. This is really formed by the action of the pyridine alone, but dimethylaniline does not produce it. It is not identical with the dibromosalicylide described by Anschütz and Robitsek (A., 1906, i, 503) or that mentioned by Earle and Jackson (*ibid.*, 177).

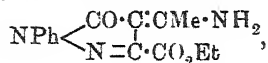
Cinnamoyl chloride gives, in the presence of pyridine, ethyl β -cinnamoylaminoacronate, in pale yellow, quadratic prisms, *m. p.* 154°, which forms a very stable dibromide, hexagonal prisms, *m. p.* 155°, and yields the known γ -aceto- β -phenylbutyric acid, or

occasionally cinnamic acid, on boiling with hydrochloric acid, evaporating to dryness, and triturating with sodium carbonate solution (evolution of ammonia). This α -ester is not changed by acetyl chloride, but a β -isomeride, m. p. 96° , is obtained by the action of ethyl cinnamate on ethyl sodioaminocrotonate. $\alpha\beta$ -Dibromo- β -phenylpropionyl chloride, m. p. 91° , only gives the corresponding propionamide.

Ethyl chloro-oxalate forms *ethyl γ -amino- α -keto- Δ^{β} -butene- $\alpha\beta$ -dicarboxylate*, $\text{NH}_2\cdot\text{CMe}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, which crystallises in hexagonal prisms, m. p. 87° (decomp.), and is hydrolysed by *N*-sodium hydroxide in the cold to the acid ester (β -amino- α -ethoxalylcrotonic acid), $\text{NH}_2\cdot\text{CMe}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, m. p. 124° (decomp.), the copper salt of which is pale green, crystallises with $2\text{H}_2\text{O}$ and decomposes at 213° . If these esters are boiled with phenylhydrazine and alcohol, the pyrazole derivative,



is formed, as a pale yellow substance, m. p. 147° , which may be hydrolysed by boiling *N*-sodium hydroxide to the free acid, m. p. 253° , the phenylhydrazine salt of which crystallises in slender needles, m. p. 129° . A different product is obtained if the phenylhydrazine is applied in 50% acetic acid solution, namely, *ethyl 1-phenyl-4- α -aminoethylidenepyrazol-5-one-3-carboxylate*,

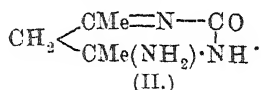
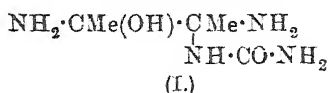


which crystallises in orange-yellow needles, m. p. 219° (decomp.). This is hydrolysed by boiling *N*-sodium hydroxide to 4-acetyl-1-phenylpyrazol-5-one-3-carboxylic acid, m. p. 242° (decomp.), which behaves on titration and towards ferric chloride as an enol, forms a product with phenylhydrazine (2 base:1 acid), m. p. 190° , and yields a compound, leaflets, m. p. 169° , when heated above its m. p.

The *N*-substituted ester isomeric with the above dicarboxylate is formed when ethyl oxalate is added to a suspension of ethyl sodioaminocrotonate in ether. *Ethyl β -ethoxalylaminocrotonate*, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, crystallises in rhombic platelets, m. p. 60° , and yields the phenylhydrazide of oxamic acid, $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$, on warming with phenylhydrazine and 50% acetic acid. The corresponding acid ester (*ethyl β -carboxalylaminocrotonate*, $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$) is found in the ethereal mother liquor from the above ester, and it may also be obtained from the ester by hydrolysis with alcoholic potassium hydroxide. It crystallises in colourless needles, m. p. 107° , and forms a compound with phenylhydrazine (1:1), m. p. 146° .

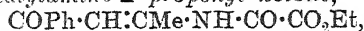
The acylacetanamines were chosen as compounds related to ethyl aminocrotonate for further studies on the action of acyl chlorides in the presence of pyridine. The following derivatives of β -amino- Δ^{α} -propenyl methyl ketone (acetylacetanamine) have been obtained

in this way: the *N*-benzoyl derivative, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{NHBz}$, large prisms, m. p. 82° (*phenylhydrazone*, silky, yellow needles, m. p. 130°); *N*-cinnamoyl derivative, silky, white prisms, m. p. 80 – 81° (*phenylhydrazone*, orange-red crystals, m. p. 148 – 149°); *N*-ethoxalyl derivative, needles, m. p. 100° ; *N*-carbethoxy-derivative, $\text{CHAc}\cdot\text{CMe}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, long, silky needles, m. p. 57° . The last-named compound reacts with liquid ammonia to form two bases, I, m. p. 206° (decomp.), and II, m. p. 72 – 74° :



The clue to the constitution of these bases is furnished by the fact that they give the known bromine derivative of acetylacetone-carbamide [4:6-dimethyldihydropyrimid-2-one] on treatment with bromine water, whilst base II changes into this carbamide on heating, with or without alcohol (compare Evans, A., 1894, i, 111).

Phenyl β-ethoxalylamino-Δ²-propenyl ketone,



silky needles, m. p. 88 – 89° , is formed in a similar manner from benzoylacetoneamine.

Acetylacetoneamine also reacts with benzenediazonium chloride to form the *benzeneazo*-compound (*β*-amino-*α*-benzeneazo-*Δ²-propenyl methyl ketone*), $\text{NPh}\cdot\text{N}\cdot\text{Cac}\cdot\text{CMe}\cdot\text{NH}_2$, slender, yellow spikes, m. p. 125° , which changes on keeping into benzeneazoacetylacetone, m. p. 90° , and yields the *phenylhydrazone* of this ketone, $\text{C}_{17}\text{H}_{15}\text{ON}_4$, as a mass of yellow needles, m. p. 185° (decomp.), when boiled with alcoholic phenylhydrazine, or 4-benzeneazo-1-phenyl-3:5-dimethylpyrazole, m. p. 62° , if heated with phenylhydrazine alone.

J. C. W.

Allylbetaine and Allylhomocholine. J. VON BRAUN and E. MÜLLER (*Ber.*, 1917, 50, 290–293).—The remarkable discovery that *N*-allylnorcodeine is physiologically antagonistic to morphine (A., 1916, i, 665) has induced the authors to investigate the influence of the introduction of an allyl group on the activity of other substances. In most cases, no such modification has been observed, but it is found that betaine and homocholine form *N*-allyl derivatives which are directly antagonistic to the parent bases, at any rate in their action on the poikilothermic heart.

Dimethyl-*γ*-hydroxypropylamine (*ibid.*, 631) combines with allyl iodide to form the quaternary *allyliodide*, m. p. 57 – 58° , from which the chloride can be made in the usual way. *Dimethyl-γ-hydroxypropylallyl ammonium chloride* (*allylhomocholine chloride*), $\text{OH}\cdot\text{C}_3\text{H}_6\cdot\text{NMe}_2(\text{C}_3\text{H}_5)\cdot\text{Cl}$, is a viscous oil, which yields a *platini-chloride*, m. p. 182° .

Methyl dimethylaminoacetate (Willstätter, A., 1902, i, 267) also forms an *allyliodide*, m. p. 83° , and this may be converted into *N*-allylbetaine, $\text{C}_3\text{H}_5\cdot\text{NMe}_2\cdot\text{CH}_2\text{CO}$, m. p. 66° , by shaking with

silver oxide and silver chloride. The base is very hygroscopic, and yields a yellowish-red *platinichloride*, m. p. 174—175°, and a soluble *aurichloride*, yellow leaflets, m. p. 146°.

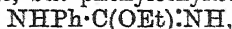
The following compounds were prepared by the usual methods, but are only briefly described, as they have no unexpected properties: 1-*Allylpyrrolidine*, volatile in steam or ether vapour; *platinichloride*, m. p. 205°, and *aurichloride*, m. p. 97—98°, both readily soluble in water. 1-*Allylthalline*, pale yellow, b. p. 176°/12 mm. 1-*Allyltheobromine*, colourless crystals, m. p. 147°. N-*Allylstrychnine*, from strychnine allyliodide by the action of silver sulphate, and then barium hydroxide. *Allyl sulphate*, from silver sulphate and allyl iodide; an unpleasant-smelling liquid which explodes on heating.

J. C. W.

Imino-esters. II. Mechanism of the Formation of Amidines. ANGELO KNORR (*Ber.*, 1917, 50, 229—236. Compare A., 1916, i, 797).—The formation of amidines by the action of ammonia on the hydrochlorides of imino-esters was explained by Pinner on the basis of the following equations: $\text{RO}\cdot\text{CR}'\text{:NH}\cdot\text{HCl} + \text{NH}_3 = \text{RO}\cdot\text{CR}'\text{:NH} + \text{NH}_4\text{Cl}$; $\text{RO}\cdot\text{CR}'\text{:NH} + \text{NH}_3 = \text{NH}_3\cdot\text{CR}'\text{:NH} + \text{R}\cdot\text{OH}$; $\text{NH}_3\cdot\text{CR}'\text{:NH} + \text{NH}_4\text{Cl} = \text{NH}_2\cdot\text{CR}'\text{:NH}\cdot\text{HCl} + \text{NH}_3$. Pinner knew, however, that ammonia had no action on free *isobutyl iminobenzoate*, and Stieglitz and his pupils have shown that this is the general rule in the case of esters of the type $\text{NH}_2\cdot\text{C}(\text{OR})\text{:NH}$, that is, the *isocarbamides*, assuming there to be, in consequence, a difference in constitution between these and the ordinary imino-esters (A., 1899, i, 359, 594). It is now found, also, that ammonia has no action on ethyl iminomethylthiolformate, $\text{OEt}\cdot\text{C}(\text{SMe})\text{:NH}$, although it reacts vigorously with the hydrochloride, the free ester, and later on guanidine hydrochloride, methyl mercaptan, and ethyl alcohol being formed. It is shown conclusively that it is ammonium chloride which reacts with the free esters to form amidine hydrochlorides, thus:



Ethyl iminoacetate and iminobenzoate, for example, react quite readily with ammonium chloride, alone or diluted with alcohol or ether, whilst the above thio-ester (A., 1916, i, 797) reacts best in alcoholic solution. Ethyl*isocarbamide* also reacts easily to form guanidine hydrochloride, but phenylethyl*isocarbamide*,



is not affected by ammonium chloride.

J. C. W.

The Simplest Organo-metallic Alkali Compounds. W. SCHLENK and JOHANNA HOLTZ (*Ber.*, 1917, 50, 262—274).—Organo-sodium and -lithium compounds have been obtained in a fairly pure state by the action of sodium on the corresponding organo-mercury compounds in light petroleum or benzene. The apparatus used was that designed for the preparation of metal ketyls (A., 1913, i, 1205), and the manipulation is fully described.

Sodium methyl, sodium ethyl, sodium n-propyl, sodium octyl, and sodium phenyl are colourless, amorphous substances, insoluble in indifferent media, which decompose without melting when heated. They inflame with violence when brought into the air, but the activity of this oxidation falls with increasing molecular weight. *Sodium benzyl*, CH_2PhNa , forms garnet-red crystals, and its ethereal solution will conduct the electric current, showing that the metallic atom is linked by a carbonium valence. It inflames in the air, yields much stilbene if the oxidation is slow, and reacts with carbon dioxide to form sodium phenylacetate.

The most convenient lithium compound to make by the above reaction is *lithium ethyl*. This crystallises from warm benzene in stout, hexagonal, limpid tablets, m. p. 95° . *Lithium methyl* and *lithium phenyl* are best prepared by mixing solutions of lithium ethyl and the mercury compounds, when they separate as white, microcrystalline precipitates, as, for example, according to the equation $2\text{LiEt} + \text{HgMe}_2 = 2\text{LiMe} + \text{HgEt}_2$. The lithium compounds inflame in the air; lithium methyl presents a fine spectacle, the flame being brilliant red accompanied by a shower of yellow sparks. J. C. W.

Resistance of the Alkyl Groups attached to a Lead Atom to the Disruptive Action of Halogens. Preparation of Mixed Lead Alkyls containing Three or Four different Radicles. GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1917, 50, 202—211. Compare A., 1916, i, 684, 800).—It has been found that when lead tetra-alkyls are treated with halogens at -75° , one alkyl group is removed, whilst at -20° a further group is lost. From the lead trialkyl haloid or lead dialkyl dihaloid so obtained, other alkyl groups can be reintroduced by the Grignard action, numerous examples having already been given. It is now stated that in all cases in which the alkyl groups are in primary attachment to the lead atom, it is the lightest group which is removed by the halogen. Working out this discovery to its logical conclusion, it has thus become possible to prepare lead tetra-alkyls with three or four different groups. As each of these can be obtained in different ways, but never as *cis-trans*-isomerides, the conclusion is drawn that the four valencies of lead are equivalent and probably arranged like those of carbon. Optical isomerism may be possible.

With the exception of the mixed lead trialkyl haloids, which do not crystallise, the compounds can all be obtained in a high degree of purity. The yields throughout are excellent. The following examples are given.

Lead dimethylethylpropyl, $\text{PbMe}_2\text{EtPr}^a$ b. p. $65^\circ/15\text{ mm.}$, D_4^{20} 1.6943, n_D^{20} 1.5110, $n_F - n_C$ 0.01687; *lead dimethylethylisobutyl*, b. p. $74^\circ/13\text{ mm.}$, D_4^{20} 1.6234, n_H 1.50327, n_D 1.50783, $n_{H\beta}$ 1.51982, n_H 1.53010, all at 20.7° ; *lead methyldiethylpropyl*, b. p. $80.8^\circ/15\text{ mm.}$, D_4^{21} 1.6403, $n_{H\alpha}$ 1.50925, n_D 1.51412, $n_{H\beta}$ 1.52638, $n_{H\gamma}$ 1.53710, at 22.1° ; *lead dimethylethylisoamyl*, b. p. $92^\circ/14\text{ mm.}$, D_4^{21} 1.5579, $n_{H\alpha}$ 1.50079, n_D 1.50524, $n_{H\beta}$ 1.51662, $n_{H\gamma}$ 1.52647, at 21.7° ; *lead methyldiethyliso-*

butyl, b. p. $87^{\circ}/13$ mm., D_4^{20} 1.5812, $n_D^{19.5}$ 1.5120, $n_F - n_C$ 0.01664; *lead methyl-diethylisoamyl*, b. p. $106^{\circ}/15.5$ mm., $D_4^{21.5}$ 1.5225, n_{Ha} 1.50336, n_D 1.50783, $n_{H\beta}$ 1.51921, $n_{H\gamma}$ 1.52934, at 20.8° ; *lead dimethylpropylisoamyl*, b. p. $105^{\circ}/15$ mm., D_4^{22} 1.5028, n_{Ha} 1.49773, n_D 1.50201, $n_{H\beta}$ 1.51313, $n_{H\gamma}$ 1.52251, at 22° ; *lead diethylpropyl-n-butyl*, b. p. $116^{\circ}/vac.$, D_4^{21} 1.4789, $n_D^{21.4}$ 1.5100, $n_F - n_C$ 0.01547 (prepared from *lead triethyl-n-butyl*, b. p. $108^{\circ}/13$ mm., $D_4^{21.5}$ 1.5285, $n_D^{21.5}$ 1.5120, $n_F - n_C$ 0.01639); *lead diethylpropylisobutyl*, b. p. $110^{\circ}/13$ mm., D_4^{21} 1.4890, n_{Ha} 1.50751, n_D 1.51195, $n_{H\beta}$ 1.52353, $n_{H\gamma}$ 1.53359, at 20° ; *lead diethylpropylisoamyl*, b. p. $127.5^{\circ}/15$ mm., $D_4^{22.1}$ 1.4892, n_{Ha} 1.50217, n_D 1.50655, $n_{H\beta}$ 1.51758, $n_{H\gamma}$ 1.52721, at 22.1° ; *lead diethylisobutylisoamyl*, b. p. $131^{\circ}/14$ mm., $D_4^{21.5}$ 1.3980, $n_D^{19.5}$ 1.5053; *lead ethylpropyl-diisoamyl*, b. p. $145.5^{\circ}/13$ mm., D_4^{21} 1.3552, $n_D^{18.5}$ 1.5039, $n_F - n_C$ 0.01524.

Lead methylethyl-n-propyl-n-butyl has b. p. $103^{\circ}/13$ mm., $D_4^{21.5}$ 1.5068, $n_D^{21.4}$ 1.5072, $n_F - n_C$ 0.01607; *lead methylethyl-n-propylisoamyl* has b. p. $115^{\circ}/15$ mm., D_4^{21} 1.4792, n_{Ha} 1.50189, n_D 1.50636, $n_{H\beta}$ 1.51747, $n_{H\gamma}$ 1.52720, at 21° ; *lead ethyl-n-propyl-n-butylisoamyl*, has b. p. $141^{\circ}/14$ mm., $D_4^{21.5}$ 1.3699, $n_D^{21.5}$ 1.5028, $n_F - n_C$ 0.01473.

The mixed lead dialkyl dihaloids are stable, crystalline salts. *Lead methylethyl dichloride*, $PbMeEtCl_2$, crystallises in filamentous needles, forms an additive compound with pyridine (very large needles), and gives precipitates of the white sulphide (soluble in hydrochloric acid or ammonium sulphide), the canary-yellow iodide, and the yellow chromate (soluble in acetic acid) when the appropriate reagents are added to its aqueous solution. *Lead ethylisoamyl dichloride* forms pearly leaflets; *lead propylisoamyl dichloride* crystallises in satiny leaflets; *lead ethylisobutyl dibromide* separates in whetstone forms; *lead n-propylisobutyl dibromide* forms bundles of satiny needles. J. C. W.

Organo-lead Compounds. VI. Lead Tetraisoamyl, Lead Tetra-isobutyl, Lead Tetra-n-propyl, and their Derivatives. GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1917, 50, 278—285. Compare, especially, A., 1916, i, 684, 800).—Some more compounds of the types PbR_4 , $PbR_3Hal.$, PbR_2Hal_2 , and PbR_3R' are described.

Lead tetraisoamyl decomposes on heating, even in a high vacuum, but may be purified by distillation in a current of steam. It is an almost odourless, colourless oil; $D_4^{21.5}$ 1.2332, n_{Ha} 1.49075, n_D 1.49457, $n_{H\beta}$ 1.50404, $n_{H\gamma}$ 1.51232, at 20.5° . *Lead triisoamyl bromide* crystallises in long, snow-white needles, m. p. $132-133^{\circ}$. *Lead diisoamyl dichloride* forms white leaflets, decomp. 108° , and the dibromide pale yellow flakes. *Lead methyltriisoamyl* has D_4^{21} 1.3134, n_{Ha} 1.49226, n_D 1.49618, $n_{H\beta}$ 1.50612, $n_{H\gamma}$ 1.51477, at 22° ; *lead ethyl triisoamyl* has $D_4^{19.5}$ 1.2922, n_{Ha} 1.49425, n_D 1.49825, $n_{H\beta}$ 1.50818, $n_{H\gamma}$ 1.51669, at 19.6° ; *lead n-propyltriisoamyl* has D_4^{22} 1.2737, n_{Ha} 1.49324, n_D 1.49703, $n_{H\beta}$ 1.50696, $n_{H\gamma}$ 1.51542, at 22° ; *lead isobutyl-triisoamyl* has $D_4^{19.5}$ 1.2522, n_{Ha} 1.49242, n_D 1.49618, $n_{H\beta}$ 1.50597, $n_{H\gamma}$ 1.51428, at 19.5° . These oils are all purified by distillation in

steam, followed by warming under reduced pressure in an atmosphere of hydrogen.

Lead tetraisobutyl crystallises in white leaflets, m. p. -23° (corr.), $D_4^{20.2}$ 1.3240, n_{H_a} 1.50004, n_D 1.50416, $n_{H\beta}$ 1.51461, $n_{H\gamma}$ 1.52375, at 20.2° . *Lead triisobutyl chloride* forms long needles, m. p. 122° (decomp.), the *bromide* crystallises in very long, glistening needles, m. p. $107-108^{\circ}$, and the *iodide* forms unstable, yellow leaflets. *Lead diisobutyl dichloride* crystallises in white leaflets, decomp. above 100° , and the *dibromide* in pale yellow leaflets, decomp. $102-103^{\circ}$. *Lead diisobutyl chlorobromide*, $Pb(C_4H_9)_2ClBr$, prepared by the action of bromine on lead triisobutyl chloride, crystallises in hard, compact, very long, flat, glistening spikes, decomp. 110° . *Lead methyltriisobutyl* has b. p. $121^{\circ}/12$ mm. (slight decomp.), $D_4^{19.3}$ 1.3977, n_{H_a} 1.49883, n_D 1.50321, $n_{H\beta}$ 1.51397, $n_{H\gamma}$ 1.52324, at 19.6° ; *lead ethyltriisobutyl* has $D_4^{22.1}$ 1.3758, n_{H_a} 1.50134, n_D 1.50552, $n_{H\beta}$ 1.51636, $n_{H\gamma}$ 1.52573, at 22.1° ; *lead n-propyltriisobutyl* has $D_4^{19.6}$ 1.3505, n_{H_a} 1.50148, n_D 1.50561, $n_{H\beta}$ 1.51631, $n_{H\gamma}$ 1.52554, at 19.6° ; *lead triisobutylisoamyl* has $D_4^{20.6}$ 1.2976, n_{H_a} 1.49696, n_D 1.50097, $n_{H\beta}$ 1.51118, $n_{H\gamma}$ 1.51989, at 20.6° .

Lead methyltri-n-propyl has b. p. $106^{\circ}/13$ mm., $D_4^{22.3}$ 1.5220, n_{H_a} 1.50456, n_D 1.50911, $n_{H\beta}$ 1.52059, $n_{H\gamma}$ 1.53058, at 22.3° ; *lead ethyltri-n-propyl* has b. p. $118.2^{\circ}/14$ mm., $D_4^{21.3}$ 1.4846, n_{H_a} 1.50703, n_D 1.51149, $n_{H\beta}$ 1.52290, $n_{H\gamma}$ 1.53299, at 21.3° ; *lead tri-n-propylisobutyl* has $D_4^{22.8}$ 1.4034, n_{H_a} 1.50235, n_D 1.50673, $n_{H\beta}$ 1.51766, $n_{H\gamma}$ 1.52716, at 22.6° ; *lead tri-n-propylisoamyl* has D_4^{21} 1.3810, n_{H_a} 1.50049, n_D 1.50465, $n_{H\beta}$ 1.51535, $n_{H\gamma}$ 1.52462, at 21° .

Lead n-propylisobutyl dichloride crystallises in very stable, sparingly soluble, rounded leaflets, and *lead isobutylisoamyl dibromide* forms elongated, transparent, pale yellow leaflets, decomp. 95° .

[All the densities recorded in this and the preceding paper are reduced to vacuum standard.]

J. C. W.

Optical Activity of Low Temperature- and Generator-coal Tars. FRANZ FISCHER and W. GLUUD (*Ber.*, 1917, 50, 111-115).—In a recent communication (*A.*, 1916, i, 800), Pictet, Ramseier, and Kaiser reported that they had obtained optically active substances from coal by extraction with benzene, but not by distillation in a vacuum. They concluded, therefore, that the coal had not experienced a temperature as high as 450° during its formation. In connexion with other work, however, the present authors have observed optical activity, beyond the limits of experimental error, with extracts of tars obtained from coals of the same origin (Saar and Lower Rhine) by low temperature ($450-550^{\circ}$) and generator processes. The isolation of the most active fractions is described; they are insoluble in acids, alkalis, or liquid sulphur dioxide.

J. C. W.

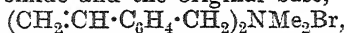
Preparation of o-Chlorotoluene. BADISCHE ANILIN- & SODA-FABRIK. (D.R.-P., 294638; from *J. Soc. Chem. Ind.*, 1917, 36, 286).—Toluene-*p*-sulphonic acid or its chloride or amide is dissolved in

sulphuric acid, the solution treated with chlorine, and the sulphonic group removed from the resulting *o*-chlorotoluene-*p*-sulphonic acid, for example, by heating it in a current of steam.

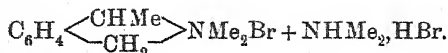
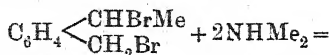
H. W.

***o*-Vinylbenzyl Bromide and its Derivatives.** J. VON BRAUN (*Ber.*, 1917, 50, 45—49).—A mixture of *o*-vinylbenzyl bromide and 1-cyanopiperidine was recently described as the product of the action of cyanogen bromide on 1-*o*-vinylbenzylpiperidine (this vol., i, 169). Attempts to isolate the former substance from the mixture have been unsuccessful, and therefore choice was made of *o*-vinylbenzyl dimethylamine (Emde, A., 1912, i, 801) as a source, for this would yield as a second product a cyanoamine of much lower b. p. or one soluble in acids.

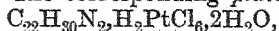
o-Vinylbenzyl dimethylamine is best obtained by distilling dimethyltetrahydroisoquinolinium hydroxide under reduced pressure. It reacts vigorously with cyanogen bromide in ethereal solution, giving the desired bromide and cyanodimethylamine in the solution and a small deposit of a *quaternary bromide* compounded of the bromide and the original base,



m. p. 178—179°. The cyanodimethylamine is extracted from the ethereal solution by means of a dilute acid, leaving *o*-vinylbenzyl bromide as a colourless, mobile, heavy oil, b. p. 119—120°/17 mm. As a benzyl bromide derivative, it has the characteristic irritating odour, and reacts readily with water, alcohol, amines, sodiomalonic esters, etc., giving products which will be described later. As a derivative of styrene, it polymerises even in the dark, and combines directly with hydrogen (Paal's method), halogens, or halogen hydrides. *o*-Ethylbenzyl bromide has b. p. 120—121°/23 mm. *o*- α -Dibromoethylbenzyl bromide crystallises in stout prisms, m. p. 46°. *o*- α -Bromoethylbenzyl bromide, obtained by shaking the unsaturated bromide with fuming hydrobromic acid, is a snow-white, crystalline mass, m. p. 36—37°, which reacts with dimethylamine according to the equation



The *quaternary bromide*, silvery leaflets, m. p. 216°, is precipitated from the aqueous solution of the mixture by the addition of alkali hydroxide. The corresponding *platinichloride*,



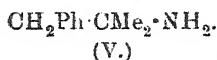
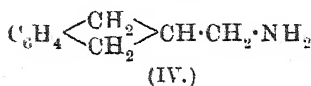
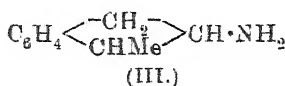
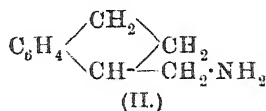
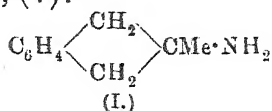
crystallises in leaflets, m. p. 201°.

o-Ethylbenzyl bromide can also be obtained from 1-*o*-ethylbenzylpiperidine. This base is prepared by reducing the corresponding vinyl compound (*loc. cit.*); it has b. p. 147°/18 mm., and forms a *hydrochloride*, leaflets, m. p. 212—213°, an *aurichloride*, m. p. 158°, a *picrate*, and a *methiodide*, m. p. 145—146°. The base reacts with cyanogen bromide to give a mixture of 1-cyano-

piperidine and *o*-ethylbenzyl bromide, and the latter can be isolated by boiling the oil with hydrobromic acid until the former is hydrolysed and dissolved.

J. C. W.

The Indene Series. IV. J. VON BRAUN, E. DANZIGER, and Z. KOEHLER (*Ber.*, 1917, **50**, 56—64. Compare this vol., i, 130).—For comparison with 2-amino-2-methylhydrindene, (I), the authors have synthesised the isomerides, (II, III, and IV), and have attempted to prepare the nearly related aromatic-aliphatic base, (V):



The corresponding alcohols are also described.

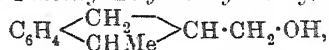
1-Hydrindylmethylamine, (II).—*α*-Hydrindone is condensed with ethyl bromoacetate in the presence of zinc to form *ethyl 1-hydrindylideneacetate*, as a viscous oil, b. p. 166—168°/10 mm. This ester yields a resin if warmed with sodium hydroxide, and 1-methylindene if hydrolysed by dilute sulphuric acid. If it is purified by shaking with sodium hydroxide and then fractionating, it yields on reduction by the Paal-Skita method only 1-methylhydrindene, b. p. 182—183°, D_4^{16} 0.9661, n_D 1.53938, but if it is first fractionated, treated with alkali to remove a minute trace of bromine, redistilled, and then reduced, it gives the normal product, *ethyl 1-hydrindylacetate*, as a pleasant-smelling, limpid oil, b. p. 149—150°/12 mm. The saturated ester can be readily hydrolysed to 1-hydrindylacetic acid, glistening leaflets, m. p. 60—61°, and this converted into the *chloride*, b. p. 146°/11 mm., which condenses readily with aromatic hydrocarbons, etc., but does not undergo internal condensation under the influence of aluminium chloride. The *amide*, m. p. 90°, is prepared from the chloride, and the *hydrazide*, matted needles, m. p. 113° (*hydrochloride*, m. p. 208°), by the action of hydrazine hydrate on the ester. Finally, 1-hydrindylmethylamine, (II), is obtained by the Hofmann reaction, or, better, from the hydrazide, through the urethane, as a colourless liquid, b. p. 125—126°/13 mm., with a not very intense odour. It forms a *hydrochloride*, m. p. 212—214°, a *platinichloride*, decomp. 235°, and a *picrate*, m. p. 176—177°.

β-1-Hydrindylethyl alcohol, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH} \end{array}$, b. p. 150—152°/11 mm., is prepared by the reduction of ethyl

1-hydrindylacetate with sodium and alcohol. Unlike the open aromatic-aliphatic alcohols, it is an almost odourless, syrupy liquid, and the corresponding β -1-hydrindylethyl chloride, b. p. 132—134°/14 mm., has a much fainter odour than the homologues of benzyl chloride.

2-Amino-1-methylhydrindene, (III).—1-Methylhydrindene-2-carboxylic acid is obtained from ethyl benzylacetoacetate (Roser, A., 1888, 1303). The chloride, b. p. 150°/20 mm., is converted into the amide, m. p. 130°, and this into 2-amino-1-methylhydrindene, b. p. 108—110°/11 mm., by Hofmann's method. The base forms a hydrochloride, m. p. 202°, a picrate, m. p. 239°, and a benzoyl derivative, m. p. 137°.

Ethyl 1-methylhydrindene-2-carboxylate, b. p. 150—151°/11 mm., may be reduced to 1-methyl-2-hydrindylmethyl alcohol,



an odourless, viscous oil, b. p. 148—150°/11 mm., the corresponding chloride having b. p. 135—138°/11 mm.

2-Hydrindylmethylamine (IV).—This base was already known (Kenner, T., 1914, 105, 2696). It forms a picrate, m. p. 180—182°, a benzoyl derivative, m. p. 120—121°, and a salicylidene compound, m. p. 66°.

β -Chloroisomylbenzene (Klages, A., 1904, i, 497) is practically indifferent towards ammonia or amines at the ordinary temperature, and under drastic treatment yields $\beta\beta$ -dimethylstyrene (*ibid.*).

J. C. W.

The State of Saturation of the Unsaturated Linking. I. H. LEY (*Ber.*, 1917, 50, 243—250).—It is a well-known fact that the additive capacity of a compound with an ethylenic linking is greatly influenced by the nature of the atoms or groups attached to the doubly linked carbon atoms. For example, styrene and stilbene readily unite with bromine, but tetraphenylethylene does not. It is common to offer the suggestion that such a difference as this is due to steric hindrance, but the author prefers to account for the facts by assuming changes to take place in the degree of saturation of the ethylene linking. He proposes to develop his arguments on the basis of electroatomic theories, the usual valency ideas being obviously insufficient.

The absorption spectra reveal also, even in cases where arguments on steric lines cannot hold, that the degree of saturation can be modified considerably by apparently small changes. The spectrum of stilbene, for example, is distinctly modified by the presence of a methyl group (α -methylstilbene) in the direction of that of the fully saturated, closely related compound, dibenzyl. The spectra of cinnamic acid and α - and β -methylcinnamic acids show similar relationships. Phenylstilbene, α -phenylcinnamic acid, and α -methylstyrene are mentioned in the same connexion, but exact quantitative comparisons will apparently be made later on, and a full discussion raised then.

The extinction coefficients of comparable solutions of the addi-

tive compounds of stilbene and α -methyl- and α -phenyl-stilbene with *s*-trinitrobenzene have also been roughly determined. In agreement with Werner's rule, that such molecular compounds possess deeper colours the more unsaturated the hydrocarbon is (A., 1910, i, 20), the conclusion must be drawn that stilbene is the most unsaturated of the three.

This effect of the introduction of an alkyl radicle is quite the opposite when the group enters a cyclic system, for it is well known that in respect of absorption and formation of molecular compounds, toluene and hexamethylbenzene behave as more unsaturated compounds than benzene (compare Werner, *ibid.*, and Pfeiffer, A., 1914, i, 551). J. C. W.

The Bucherer Reaction. HARTWIG FRANZEN and HUBERT KEMPF (*Ber.*, 1917, 50, 101—104).—The Bucherer reaction, whereby amines can be converted into phenols through the action of sulphites (A., 1902, i, 718; 1903, i, 627; 1904, i, 309; 1905, i, 48, 585; 1907, i, 509; 1908, i, 455; 1909, i, 521, 787; 1910, i, 144), is fundamentally a process of hydrolysis, according to the equation $\text{ArNH}_2 + \text{H}_2\text{O} = \text{ArOH} + \text{NH}_3$. Regarded in this light, it is remarkable that a reaction which is notoriously difficult of achievement by the strong mineral acids should be brought about by sulphurous acid. The authors have therefore made some comparative tests on the hydrolysis of the naphthylamines and naphthionic acid by hydrochloric, sulphuric, phosphoric, phosphorous, boric, arsenious, hypophosphorous, and sulphurous acids, using as the criterion the amount of ammonia developed after one, two, three, or four days. As only the last two acids produce any notable effects, the others being about equally indifferent, the conclusion is drawn that the hydrolysis of aromatic amines is governed by the degree of unsaturation rather than by the strength of the acid. J. C. W.

Benzyltetramethylammonium. W. SCHLENK and JOHANNA HOLTZ (*Ber.*, 1917, 50, 274—275).—When a solution of sodium benzyl (this vol., i, 256) in cold ether is shaken with dried tetramethylammonium chloride in an atmosphere of nitrogen, *benzyltetramethylammonium*, $\text{CH}_2\text{Ph}\cdot\text{NMe}_4$, is formed, as a brilliant red, granular powder (compare the analogous preparation of triphenylmethyltetramethylammonium, A., 1916, i, 385). This is either insoluble in or decomposed by ordinary solvents, even pyridine, and is hydrolysed by water to toluene and tetramethylammonium hydroxide. J. C. W.

Ammonium Compounds of a New Type. W. SCHLENK and JOHANNA HOLTZ (*Ber.*, 1917, 50, 276—278).—If an ethereal solution of potassiumdi-*p*-tolylamine (A., 1914, i, 823) is shaken with dried tetramethylammonium chloride in an atmosphere of nitrogen, *di-p-tolylaminotetramethylammonium*, $\text{Me}_4\text{N}\cdot\text{N}(\text{C}_7\text{H}_7)_2$, is formed. This crystallises from pyridine in greenish-yellow leaflets, which soon become brown in the air, and is hydrolysed by water to ditolylamine and tetramethylammonium hydroxide. Although the two nitrogen atoms are linked together, the sub-

stance is therefore a salt, which is of considerable interest in connexion with the function and distribution of the fifth valence of nitrogen. The pyridine solution is also an electrolyte, the equivalent conductivity being = 5.72.

Diphenylaminotetramethylammonium is a very similar substance, crystallising in greenish-yellow needles. J. C. W.

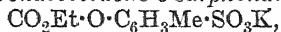
Phenol Bases. III. J. VON BRAUN and E. DANZIGER (*Ber.*, 1917, 50, 286—289).—The introduction of a phenol group in the para-position in β -phenylethylamine and homologous bases is known to have the effect of increasing their physiological activity, but such seems not to be the case with 2-amino-2-methylhydrindene (this vol., i, 130). The new phenolic base has been prepared through the nitro-, amino-, and hydroxy-derivatives of 2-acetyl-amino-2-methylhydrindene.

5-Nitro-2-acetyl-amino-2-methylhydrindene, the sole product of the action of fuming nitric acid at 0°, has m. p. 144—145°; 5-amino-2-acetyl-amino-2-methylhydrindene has m. p. 153—154°, and forms an unstable, white hydrochloride, a *picrate*, m. p. 215°, and a *benzoyl* derivative, m. p. 206°; 2-acetyl-amino-5-hydroxy-2-methylhydrindene has m. p. 112°; and 2-amino-5-hydroxy-2-methylhydrindene, $\text{OH}\cdot\text{C}_6\text{H}_5\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{CMe}\cdot\text{NH}_2$, is a very pale pink, microcrystalline powder, m. p. 154°, which yields a very soluble hydrochloride, a red *platinichloride*, m. p. 229°, a *picrate*, m. p. 240°, and a *dibenzoyl* derivative, m. p. 180°.

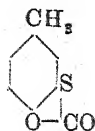
5-Nitro-2-amino-2-methylhydrindene is an oily base, which forms a *hydrochloride*, and a *picrate*, m. p. 220°. J. C. W.

3-Thiol-*p*-cresol. TH. ZINCKE and K. ARNOLD (*Ber.*, 1917, 50, 116—126).—3-Thiol-*p*-cresol has been known hitherto only in the form of bromine derivatives (*A.*, 1911, i, 287). It has now been isolated, and a number of related compounds prepared.

An alkaline solution of potassium *p*-cresol-3-sulphonate (*ibid.*) is shaken with ethyl chloroformate, and thus converted into potassium 4-ethylcarbonatotoluene-3-sulphonate,

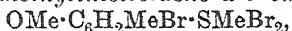


which crystallises in long needles. The corresponding *sulphonyl chloride*, large, stout crystals, m. p. 59°, may be converted into the *sulphonanilide*, m. p. 126°, or reduced by means of zinc dust and alcohol to the mercaptan. Only a trace of the mercaptan can actually be isolated, as it is very unstable. The main products are the oxidation product, 4-ethylcarbonatotolyl 3-disulphide, $(\text{CO}_2\text{Et}\cdot\text{O}\cdot\text{C}_6\text{H}_3\text{Me})_2\text{S}_2$, stout crystals, m. p. 73°, and the carbonate (annexed formula), long spikes, m. p. 83°. This carbonate may be hydrolysed by aqueous-alcoholic sodium hydroxide to 3-thiol-*p*-cresol, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SH}$, which is a limpid liquid, b. p. 110—112°/18 mm., with a peculiar, not unpleasant odour. The *dibenzoate* forms colourless needles, m. p. 86°.

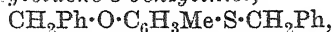


A number of ethers of 3-thiol-*p*-cresol, and their

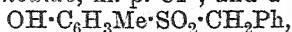
bromination and oxidation, are described. Methyl iodide reacts in the presence of sodium methoxide to form 3-methylthiol-*p*-cresol, b. p. 118—120°/18 mm., which yields 2:5-dibromo-3-methylthiol-*p*-cresol dibromide (*ibid.*) when treated with bromine. Methyl sulphate gives the dimethyl ether, 4-methoxy-3-methylthioltoluene, b. p. 145—150°/39 mm., which reacts with bromine to form 5-bromo-4-methoxy-3-methylthioltoluene dibromide,



in dark reddish-brown needles, and this is readily converted into 5-bromo-4-methoxy-3-methylthioltoluene, colourless needles, m. p. 63—64°, when shaken with sodium hydrogen sulphite. Benzyl chloride reacts in the presence of alkali to form the two benzyl ethers. 4-Benzylxytoluene-3-benzylthiol,



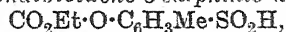
forms colourless needles, m. p. 85°, and may be oxidised in glacial acetic acid solution by means of perhydrol to the sulphoxide, slender needles, m. p. 106—107°, and then to the sulphone, long, white needles, m. p. 138°. 3-Benzylthiol-*p*-cresol, b. p. 190—192°/21 mm., yields an acetate, slender needles, m. p. 63°, and may also be oxidised to a sulphoxide, m. p. 84°, and a sulphone,



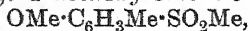
stout prisms, m. p. 146°, the acetate of which forms colourless leaflets, m. p. 128°.

If 3-thiol-*p*-cresol or either of its benzyl ethers is treated with bromine, 2:4-dibromo-*p*-cresol 3-disulphide, $(\text{OH}\cdot\text{C}_6\text{HMeBr}_2)_2\text{S}_2$, is formed, in stout, pale yellow crystals, m. p. 174—175°; the acetyl derivative has m. p. 163°.

When a mixture of ethylcarbonato-*p*-cresol-3-sulphonyl chloride and sodium hydrogen carbonate is added to a solution of sodium sulphite, 4-ethylcarbonatotoluene-3-sulphinic acid,



is formed, in stout, monoclinic prisms, m. p. 102°. This yields a methyl ester (from the silver salt), glistening prisms, m. p. 121°, and may be hydrolysed to *p*-cresol-3-sulphinic acid, a very hygroscopic mass which gives a deep blue colour in concentrated sulphuric acid. Methyl 4-methoxytoluene-3-sulphinate,



long needles, m. p. 88°, is obtained by treating this acid with methyl sulphate or by oxidising the above 4-methoxy-3-methylthiol-toluene.

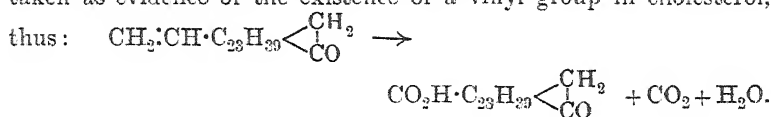
J. C. W.

***p*-Phenetyltellurium Compounds.** KARL LEDERER (*Ber.*, 1917, 50, 238—243).—The author suggested that compounds which Rohrbach described as di-*p*-anisyl and di-*p*-phenetyl tellurides were really methylene compounds (A., 1916, i, 208) and has already given an account of the true di-*p*-anisyl telluride (*ibid.*, 647). Di-*p*-phenetyl telluride, $\text{Te}(\text{C}_6\text{H}_4\cdot\text{OEt})_2$, is prepared by the action of tellurium dibromide on magnesium *p*-phenetyl bromide. It crystallises in matted needles, m. p. 63°, b. p. 235—240°/18 mm., and forms the following additive compounds with the mercuric haloids; chloride, elongated, quadrilateral platelets, m. p. 150—151°;

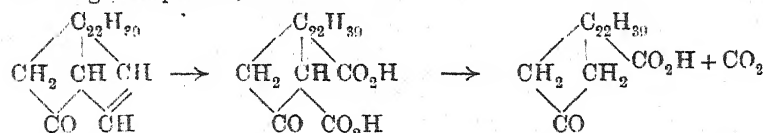
bromide, iridescent scales, m. p. 155—156°; iodide, a yellow powder, m. p. 123—124°. The *di-p-phenetyltelluronium* compounds described are the *dichloride*, $(C_6H_4 \cdot OEt)_2TeCl_2$, needles, m. p. 125°; *dibromide*, four-sided columns from ether or scales from alcohol, m. p. 116—117°; *di-iodide*, ruby-red crystals, m. p. 134—135°; *oxide*, m. p. 135—148° (indefinite); and *methiodide*, m. p. 69°.

Phenyl-*p*-tolyltelluronium oxide (*ibid.*, 810) has m. p. 154—155°.
J. C. W.

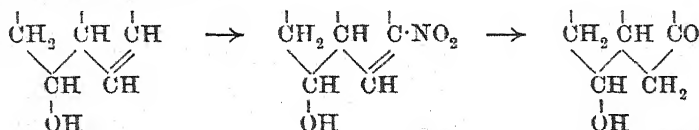
Cholesterol. XXV. A. WINDAUS (*Ber.*, 1917, 50, 133—137).—When the ketone corresponding with cholesterol, namely, cholestenone, is oxidised with potassium permanganate, a monobasic ketonic acid is formed (A., 1906, i, 579). This was originally supposed to have the formula $C_{26}H_{42}O_3$, and its production was taken as evidence of the existence of a vinyl group in cholesterol,



It is now found, however, that the acid really has the formula $C_{26}H_{44}O_3$, which destroys the accepted view that cholesterol has an unsaturated group at the end of a chain. The ethylene linking can only be in a ring, in such a position that a β -ketonic dicarboxylic acid and then a ketonic monocarboxylic acid is formed when the ring is ruptured, thus:



Further evidence in support of this view is now recognised in the established fact that cholesterol can be nitrated and the nitro-compound reduced by means of zinc and acetic acid to a ketone-alcohol, cholestanonol (A., 1904, i, 49). This recalls the conversion of indene into nitroindene and then into β -hydrindone, and may be formulated thus:



Cholestanonol may be reduced by sodium and alcohol to *cholestandiol*, $C_{27}H_{46}O_2$, leaflets and prisms, m. p. 216°, which yields a *diformate*, long needles, m. p. 150°, and may be converted by means of phosphorus pentachloride into the corresponding *dichlorocholestane*, hexagonal leaflets, m. p. 128°. This forms β -cholestane when boiled with sodium and amyl alcohol, but this hydrocarbon can be obtained much more readily from cholestanonol derivatives

(cholestandione, oxycholestenone, β -cholestanone, etc.) by reduction with amalgamated zinc and hydrochloric acid (Clemmensen's method). J. C. W.

Transformation of α -Glycols. F. COMA Y ROCA (*Anal. Fis. Quim.*, 1917, 15, 29—50).—An investigation of the influence of the methoxyl group on the transformation of α -glycols. *α -Phenyl- $\alpha\beta$ -di-*p*-anisylethylene glycol*, prepared by the interaction of *p*-anisoin and magnesium phenyl bromide, forms colourless crystals, m. p. 163—168°. Sulphuric acid of 30% strength converts it into *phenyl-di-*p*-anisylacetaldehyde*, colourless crystals, m. p. 88—89°, which yields an *oxime*, m. p. 132—133°, and a *semicarbazone*, m. p. 186—187°, and is converted by alcoholic potash into *phenyldi-*p*-anisylmethane*, colourless crystals, m. p. 100—101°.

*γ -Phenyl- $\alpha\beta$ -di-*p*-anisylpropylene glycol* is obtained from *p*-anisoin and magnesium benzyl chloride, and forms crystals, m. p. 152—153°. It is converted by 30% sulphuric acid into *β -phenyl- $\alpha\alpha$ -di-*p*-anisylpropaldehyde*, colourless crystals, m. p. 71—72°, which yields an *oxime*, colourless crystals, m. p. 116—118°, and is transformed by alcoholic potash into *α -phenyl- $\beta\beta$ -di-*p*-anisylethane*, crystals, m. p. 89—90°.

*Di-*p*-anisylbenzylcarbinol*, m. p. 140—141°, is prepared by the action of magnesium benzyl chloride on di-*p*-anisyl ketone, and is converted by acetyl chloride into *α -phenyl- $\beta\beta$ -di-*p*-anisylethylene*, m. p. 61—62°, which is reduced by sodium and alcohol to *phenyl-di-*p*-anisylethane*.

Magnesium isobutyl bromide and amygdalic acid yield *α -phenyl- $\beta\beta$ -diisobutylethylene glycol*, m. p. 72—73°. With magnesium isoamyl bromide the product is *α -phenyl- $\beta\beta$ -diisoamylethylene glycol*, needles, m. p. 109—110°.

The interaction of *p*-anisole and magnesium phenyl bromide, expected to yield diphenyldi-*p*-anisylethylene glycol, formed a *substance*, m. p. 164—165°, and another *substance*, m. p. 174—175°, separable by fractional crystallisation.

The dehydration of glycols containing methoxyl produces aldehydes; that of other glycols yields ketones. A. J. W.

Spectrochemistry of Benzene Derivatives. Cinnamic Esters. Hydroxystyrenes and their Ethers. K. VON AUWERS (*Annalen*, 1917, 413, 253—309).—In his researches to determine the influence of ring formation on the spectrochemical behaviour of organic compounds, the author has been led to compare definite groups of substances, for example, the esters of cinnamic acids with those of coumarilic acids and certain styrene derivatives with coumarones and coumaranones. The results of these comparisons will be given in a later paper, the purpose of the present communication being to ascertain how far the spectrochemical regularities which have been determined for the simpler aromatic compounds are applicable to compounds of partly different structure. In comparing different compounds the author, according to his usual custom, employs the specific exaltation, $E\Sigma$, as the typical and characteristic spectrochemical value.

Esters of Cinnamic Acids.—The methyl and ethyl esters of thirteen cinnamic acids containing methyl or ethyl groups as substituents have been examined. It is found that the substituents, as usual, influence the spectrochemical behaviour of the parent substance according to their position. Situated in the side-chain, they depress the exaltation of the optical constants, the ethyl group in many instances more so than the methyl. Particularly noticeable is the depressing influence of two such alkyl groups, the specific exaltations of ethyl cinnamate being lowered to one-third or one-fourth of their value in the $\alpha\beta$ -dimethylcinnamate and $\alpha\beta\gamma$ -trimethylcinnamate. A methyl group in the para-position generally increases the exaltation; in the ortho-position it does not change the exaltation of the dispersion, but slightly depresses the exaltation of the specific rotation.

The influence of a methoxy-substituent in an alkyl cinnamate is not so simple as in the case of the benzene molecule. The variation of its influence on the exaltation with its position is different according as the cinnamate does or does not contain a methyl group in the α - or β -position, and the original must be consulted for details, and also for the variations of the exaltations of six pairs of stereoisomeric cinnamates and of various styrene derivatives.

The following new compounds are described: *Propyl coumarate*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Pr}$, clusters of colourless needles, m. p. $71-72^\circ$, prepared from the silver salt and propyl iodide in boiling ether. *Methyl α -p-dimethylcinnamate*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}:\text{CMe}\cdot\text{CO}_2\text{Me}$, prepared by condensing *p*-tolualdehyde and methyl propionate, is an oil, b. p. $151^\circ/14$ mm., D_4^{25} 1.0507, n_D 1.55635, n_D 1.56400, n_B 1.58432, and n_γ 1.60362 at 18.3° ; the free acid forms colourless needles, m. p. $169-170^\circ$. *Methyl 6-methoxy- α -3-dimethylcinnamate*, $\text{C}_{13}\text{H}_{16}\text{O}_3$, prepared in a similar manner from 6-methoxy-*m*-tolualdehyde, is an oil, b. p. $168^\circ/11$ mm., D_4^{25} 1.0989, n_D 1.55727, n_D 1.56424, and n_B 1.58477 at 14.6° ; the free acid forms stout prisms, m. p. 122° . *6-Methoxy- β -3-dimethylcinnamic acid*, $\text{C}_{12}\text{H}_{14}\text{O}_3$, felted needles, m. p. $113-115^\circ$, prepared from the crude ester obtained from β -5-dimethyl-*o*-coumaric acid and methyl sulphate, yields a pure methyl ester, stout prisms, m. p. 36° , b. p. $163.2-164.4^\circ/11$ mm., D_4^{27} 1.0872, n_D 1.54083, n_D 1.54716, n_B 1.56290, and n_γ 1.57804 at 12.7° , n_D^{20} 1.5439. *o-Methoxystyryl methyl ketone*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{COMe}$, large prisms, m. p. $48-50^\circ$, b. p. $180-182^\circ/20$ mm., is obtained from the *o*-hydroxy-compound, 2*N*-sodium hydroxide, and methyl sulphate; it has D_4^{14} 1.0534, n_D 1.57525, n_D 1.58591, n_B 1.61640 at 61.4° . *β -Acetoxy- α -methylstyrene*, $\text{CPhMe}\cdot\text{CH}\cdot\text{OAc}$, prepared by boiling hydratropaldehyde with acetic anhydride and anhydrous sodium acetate, is an oil having $D_4^{15.2}$ 1.0574, n_D 1.53680, n_D 1.54278, n_B 1.55801, and n_γ 1.57204 at 15.2° .

β -Bromo- β -o-tolylpropionic acid, $\text{C}_{10}\text{H}_{11}\text{O}_2\text{Br}$, stout prisms, m. p. $125-126^\circ$, obtained by treating *o*-methylcinnamic acid with hydrobromic acid (saturated at 0°) first in the cold and then at the ordinary temperature, is converted by warm sodium carbonate solution into an oil, the greater part of which polymerises on distil-

lation, but the portion which distills is *o*-methylstyrene, an oil with a sweet odour, b. p. $55.4^{\circ}/12$ mm., D_{13}^{25} 0.9168, n_D 1.54219, n_D 1.54817, n_B 1.56499, and n_y 1.58003 at 13.25° .

The reaction between magnesium methyl iodide and ethyl *m*-hydroxybenzoate in ether leads to the formation of *m*-hydroxyphenyldimethylcarbinol, $\text{OH}\cdot\text{CMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, prisms, m. p. $105\text{--}106^{\circ}$, which develops a blue coloration with aqueous ferric chloride and is converted by prolonged boiling with acetic anhydride into the acetate, $\text{C}_{11}\text{H}_{12}\text{O}_5$, b. p. $124^{\circ}/12$ mm., of 3-hydroxy- α -methylstyrene, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}\cdot\text{CH}_2$, b. p. $119^{\circ}/11$ mm., D_{13}^{20} 1.0476, n_D 1.56721, n_D 1.57337, n_B 1.59064, and n_y 1.60612 at 13.0° . The latter condenses with monochloroacetic acid in aqueous sodium hydroxide to form 3-isopropenylphenoxyacetic acid, $\text{C}_{11}\text{H}_{12}\text{O}_3$, flat needles, m. p. 98° . C. S.

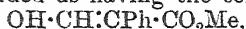
Isomerism of Formylphenylacetic Esters. IV. Methyl Formylphenylacetate. WILHELM WISLICENUS [with KURT BÖRNER, PAUL KURTZ, and ERNST A. BILHUBER] (*Annalen*, 1916, **413**, 206—252. Compare A., 1912, i, 623; 1900, i, 9, 597).—In 1894, Bishop, Claisen, and Sinclair described methyl formylphenylacetate as a viscous oil, b. p. $135\text{--}136^{\circ}/14$ mm. The authors have now thoroughly examined it. The preparation of the sodium and potassium derivatives from methyl phenylacetate, methyl formate, and sodium or potassium in absolute ether is described. Other derivatives described are the normal copper, $(\text{C}_{10}\text{H}_9\text{O}_3)_2\text{Cu}$, green crystals, m. p. $194\text{--}196^{\circ}$ (decomp.), basic copper methoxide, $(\text{C}_{10}\text{H}_9\text{O}_3)\text{Cu}\cdot\text{OMe}$, decomp. 204° , nickel compound, pale green needles with $1\frac{1}{2}\text{MeOH}$, and cobalt compound, rose needles with $1\frac{1}{2}\text{MeOH}$.

By acidifying the sodium or potassium derivative, the ester is obtained as a viscous oil, b. p. $123\text{--}125^{\circ}/12$ mm., which usually sets to a crystalline mass. The authors find that two modifications, both of which are crystalline, exist; "mixed" modifications corresponding with the β - and Michael's modifications of the ethyl ester (*loc. cit.*) do not occur.

The α -modification is prepared (1) by acidifying the copper derivative, (2) by the gradual addition of an acid to aqueous solutions of the sodium and potassium derivatives, (3) always when solutions of the ester are evaporated after being kept for some time, (4) by heating the β -modification above its m. p., and (5) by distillation of the ester under reduced pressure. It forms colourless leaflets or plates, m. p. $40\text{--}41^{\circ}$, develops in alcoholic solution with a small quantity of ferric chloride a deep bluish-violet coloration, gives a green, crystalline precipitate with a solution of copper acetate, slowly becomes blue after several minutes when shaken with de-colourised magenta solution, and reacts with phenylcarbimide to form the expected phenylcarbamate, $\text{NHPh}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}_2\text{Me}$, colourless needles, m. p. $133\text{--}134^{\circ}$. Mixed with an equal molecular quantity of aniline, it yields methyl β -anilino- α -phenylacrylate, $\text{NHPh}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}_2\text{Me}$, colourless needles, m. p. $113\text{--}114^{\circ}$, which is converted into 4-hydroxy-3-phenylquinoline at 265° with loss of

methyl alcohol. The ester reacts with *p*-xylydine to form a dark brown oil, which is converted by heating into 4-hydroxy-3-phenyl-5:8-dimethylquinoline, yellowish-white needles, m. p. 254—256°. With an alcoholic solution of phenylhydrazine at 0°, the ester yields the phenylhydrazone, $\text{NPh}\cdot\text{N}:\text{CH}\cdot\text{CHPh}\cdot\text{CO}_2\text{Me}$, stout prisms, m. p. 116—117°, together with formylphenylacetic acid hydrazide. In a similar manner, it reacts with diphenylhydrazine to form the diphenylhydrazone, $\text{NPh}_2\cdot\text{N}:\text{CH}\cdot\text{CHPh}\cdot\text{CO}_2\text{Me}$, colourless needles, m. p. 86—87°, whilst an aqueous solution of the sodium derivative of the ester reacts with semicarbazide hydrochloride to form the semicarbazone, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{CHPh}\cdot\text{CO}_2\text{Me}$, crystals, m. p. 159—160°.

In its general behaviour the α -modification behaves like a typical enol and is to be regarded as having the constitution



corresponding with the α -modification of the ethyl ester (*loc. cit.*).

The β -modification of the methyl ester can be prepared only in one way: by adding an aqueous solution of the sodium derivative as rapidly and as suddenly as possible to an excess of cold, not too dilute sulphuric acid. A spontaneous change of the α - into the β -modification has never been observed (unlike the ethyl ester, *loc. cit.*). The β -modification forms leaflets from warm benzene, m. p. 91—93°. It is much more soluble than the α -form in methyl alcohol and in water, but dissolves less readily than this in benzene and in light petroleum. A freshly prepared, cold alcoholic solution does not give a coloration with ferric chloride. The β -modification gives a precipitate with a solution of copper acetate only after long keeping (owing to change into the α -form), instantly recolours a decolorised solution of magenta, and reacts slowly and incompletely with phenylcarbimide to form the same phenylcarbamate as does the α -form.

The phenomena (decrease in the intensity of the coloration with ferric chloride; contraction in the volume of the solution) observed in an ethyl-alcoholic solution of the α -ethyl ester, which have been attributed to the change of the enol to an aldo-form, are repeated in the case of the methyl-alcoholic solution of the methyl ester. In this case, however, a definite methyl alcoholate, $\text{C}_{10}\text{H}_{10}\text{O}_3 + \text{MeOH}$, m. p. 89—92°, crystallises when the not too dilute solution is strongly cooled. The additive compound, which does not develop a coloration with ferric chloride, is formed from the β -modification after cooling the solution for one hour, but from the α -modification after twenty to twenty-four hours, and is therefore probably formed only from the β -modification. It can be recrystallised from warm benzene, but easily loses methyl alcohol by keeping in the air, by warming, and rapidly in a vacuum, the α -modification being obtained. The behaviour of an "old" methyl-alcoholic solution of the methyl ester with ferric chloride, copper acetate, and decolorised magenta solution is just what would be expected if the solution contained an alcoholate of the β -modification, which can be slowly decomposed by the reagent, yielding the α -modification. Michael and Fuller (A., 1912, i, 861) have directed attention to the

formation of additive compounds of the ethyl ester with methyl and with ethyl alcohol.

The constitutions of the two modifications of methyl formyl-phenylacetate are discussed at length. The α -form is undoubtedly an enol. The β -form presents difficulties. Some facts point to an aldo-form, others to a second, geometrically isomeric, enol form. Owing to the discovery of the alcoholates, all the evidence previously advanced in the case of the ethyl ester in favour of the aldo-form and based on the physico-chemical properties of alcoholic solutions loses in weight. On the other hand, since 1912 the properties of the true keto-forms of desmotropic substances have become better known, and in view of this knowledge the fact that the β -ester has about the same solubility in alkali hydroxide as the α -ester (A., 1912, i, 623) strengthens the view that the β -modification may be a second enol form. Moreover, Meyer has shown by his bromine method that the four modifications of the ethyl ester are unsaturated (A., 1912, i, 940), and the authors now show that both modifications of the methyl ester in freshly prepared methyl-alcoholic solution equally and almost quantitatively absorb bromine. These facts and the evidence of Scheiber and Herold's method of examination of the ethyl ester by means of ozone do not uphold the view that the β -modification is an aldo-form. Nevertheless, it must be acknowledged that the changes which characterise true aldehyde reactions, such as the restoration of the colour of decolorised magenta solution and the addition of methyl alcohol, occur more rapidly with the β - than with the α -modification. Weighing all the evidence, the authors incline at the present moment to the view that the two modifications of methyl formyl-phenylacetate (and also of the ethyl ester) are enols and examples of geometrical or *cis-trans*-isomerism, despite the facts that the β -form can under no conditions be made to develop a coloration with ferric chloride and that the two modifications behave so differently with copper acetate. C. S.

Mixed Anhydrides derived from Benzoylacrylic Acid. J. BOUGAULT (*Compt. rend.*, 1917, 164, 310—313).—A continuation of previous work (A., 1908, i, 791). The author has now condensed the two isomeric α -bromocinnamic acids with benzoylacrylic acid, by the addition of iodine in potassium iodide to a solution of their sodium salts with sodium phenylisocrotonate in the presence of sodium carbonate. The stable form gives an *anhydride*, $\text{COPh}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot\text{CBr}:\text{CHPh}$, m. p. 100°, and the labile form an isomeric *anhydride*, m. p. 125°. These anhydrides have properties similar to those of the four anhydrides previously described (*loc. cit.*). When heated at 100° with 50% acetic acid, they give benzoylacrylic acid and the respective α -bromocinnamic acids. Attempts to convert the anhydride, m. p. 125°, into the anhydride, m. p. 100°, were unsuccessful.

Further evidence is adduced in support of his theory as to the mode of formation of these anhydrides, in that γ -hydroxyphenylcrotonic acid, which is converted into benzoylacrylic acid by the

action of iodine in the presence of sodium carbonate, does not give a mixed anhydride with sodium benzoate under the above conditions, although benzoylacrylic acid is formed. W. G.

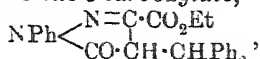
Preparation of Arylamides of 2-Hydroxynaphthalene-3-carboxylic Acid. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 294799; from *J. Soc. Chem. Ind.*, 1917, 36, 286).—A mixture of 2-hydroxynaphthalene-3-carboxylic acid with a large excess of an aromatic amine is treated with phosphorus chloride, whereby the hydroxynaphthoyl chloride first formed reacts with the amine to form the arylamide. The yield is approximately quantitative. H. W.

Desmotropic Forms in the Series of Oxalacetic Ester Derivatives, especially of Ethyl Diphenylmethyloxalacetate [α -Oxalo- $\beta\beta$ -diphenylpropionate]. WILHELM WISLICENUS and KARL EBLE (*Ber.*, 1917, 50, 250—262).—Although the enolic form of methyl oxalacetate is so much more favoured than the ketonic form that the isolation and preservation of the latter require special precautions (see Dieckmann, A., 1916, i, 820), it would appear from the usual chemical and physical measurements that the amount of the enol present in a methyl-alcoholic solution is unusually small. This is due to the fact that combination with the solvent takes place, and such an additive compound may be isolated.

It was anticipated that the ketonic form would be more stable in the case of solid esters having a heavy residue as a substituent of the methylene group, and two examples are described in which the ketonic structure is actually preferred, namely, diethyl α -oxalo- $\beta\beta$ -diphenylpropionate and diethyl α -oxalo- β -diphenylenepropionate.

Ethyl $\beta\beta$ -diphenylpropionate (the acid is made by condensing cinnamic acid with benzene in the presence of aluminium chloride) condenses with ethyl oxalate in the presence of potassium ethoxide to form the potassium compound of diethyl α -oxalo- $\beta\beta$ -diphenylpropionate, which crystallises in small rods. The unstable enol is precipitated if the solution of this salt is stirred into cold sulphuric acid; it crystallises from a benzene-light petroleum mixture in colourless, rhombic tablets, m. p. 99—101°. The ketone modification, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}(\text{CHPh}_2)\cdot\text{CO}_2\text{Et}$, is obtained by crystallising the enol from alcohol, or by the action of carbon dioxide on a solution of the potassium salt; it crystallises in bundles of long rods, m. p. 60—61°. The ester is readily hydrolysed by 20% potassium hydroxide to oxalic and diphenylpropionic acids, but is indifferent to the action of 20% sulphuric acid at 150°. It loses carbon monoxide at 200°, forming ethyl diphenylisuccinate, m. p. 57—60° (Henderson, T., 1891, 59, 731). The ester also forms an additive compound with phenylhydrazine (rhombic leaflets, m. p. 112°), which changes on heating into the phenylhydrazone, silky, yellow needles, m. p. 90—91°, and this is

further transformed by heating at 195—200° into *ethyl 1-phenyl-4-diphenylmethylpyrazol-5-one-3-carboxylate*,



which crystallises in almost colourless, rhombic leaflets, m. p. 148—149°.

The above potassium salt is very sensitive to the action of moisture, changing readily into the *potassium salt of ethyl α-oxalo-ββ-diphenylpropionate*, $\text{CO}_2\text{K}\cdot\text{CO}\cdot\text{CH}(\text{CHPh}_2)\cdot\text{CO}_2\text{Et}\cdot\text{H}_2\text{O}$, which crystallises in bundles of filaments, m. p. 200° (decomp.). The free ester acid may be obtained from this salt or by shaking the above enolic or ketonic ester with 10% sodium carbonate until dissolution takes place, and then acidifying. It has m. p. 96—97° and crystallises from benzene with $\frac{1}{2}\text{C}_6\text{H}_6$, m. p. 90—92°. It also forms a *phenylhydrazone*, greenish-yellow needles, m. p. 190—192°, which changes on heating at 190—200° into *1-phenyl-4-diphenylmethylpyrazol-5-one*, prisms or leaflets, m. p. 220—221° (compare the above pyrazolone).

Fluorene-9-acetic acid may be prepared in one operation, starting with fluorene, ethyl oxalate, and ethyl bromoacetate (compare Mayer, A., 1913, i, 1171). It crystallises in flat, silky needles, m. p. 138—139°. The *ethyl ester*, b. p. 214°/12 mm., condenses with ethyl oxalate in the presence of potassium ethoxide to form the *potassium compound of diethyl α-oxalo-β-diphenylenepropionate*, which crystallises in colourless needles. The free ester, $\text{C}_6\text{H}_4 > \text{CH}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, can be obtained as an enol, but it changes even by crystallisation from cold benzene into the ketonic form, which separates in bundles of needles, m. p. 86—88°.

J. C. W.

Occurrence of Mellitic Acid. EDMUND O. VON LIPPMANN (*Ber.*, 1917, 50, 236—238).—Some years ago (A., 1895, i, 164) the author reported the occurrence of mellitic acid in a black, humus-like deposit found in a disused conduit in a sugar refinery. When an old copper conduit was dismantled recently, a similar deposit was found.

In connexion with the author's view that the formation of mellitic acid represents a gradual, but thorough, process of oxidation, another accidental production of large crystals of aluminium mellitate, $\text{C}_{12}\text{H}_{12}\text{Al}_2\cdot 18\text{H}_2\text{O}$, "honey stone," is reported. A load of aluminous sludge from a plant for sewage treatment was deposited on a heap of brown coal rubbish, on the top of which a small plank was lying. After two years, when the refuse was being removed, the crystals of "honey stone" were found in a hollow under the wood.

J. C. W.

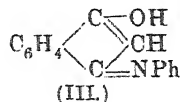
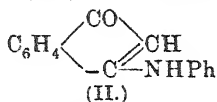
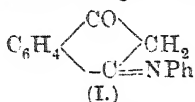
Preparation of Protocatechualdehyde. L. SCHMIDT (D.R.-P., 295337, addition to D.R.-P., 278778; from *J. Soc. Chem. Ind.*, 1917, 36, 306).—The piperonal diacetate, obtained from piperonal

as described in the original patent (A., 1915, i, 682), is treated with chlorine, and the resulting dichloropiperonal diacetate is decomposed with water. Derivatives of chloroacetic acid are not formed during the chlorination.

H. W.

Indandione and Bindone. I. Aniline Derivatives of Indandione. WILHELM WISLICENUS and HUGO PFANNENSTIEL (*Ber.*, 1917, 50, 183—189).—The condensation products of indandione (diketohydrindene) and bindone (anhydrobisdiketohydrindene) can be resolved by treatment with aniline into simple derivatives of indandione. As a preliminary to a series of communications on this reaction, the anils of indandione are now described.

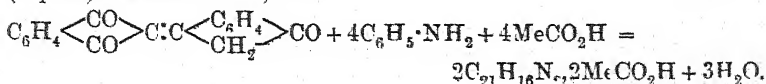
If indandione is dissolved in warm aniline and dilute acetic acid is added to the cold solution, *indandione monoanil* (I) soon separates, in yellowish-green, rectangular leaflets, m. p. 208° (decomp.). This forms unstable salts with mineral acids, in which it conforms to type (II), and also with alkali hydroxides, in which the remaining structure, (III), is probable.



Schlossberg (*A.*, 1900, i, 665) ascribed to the free substance formula (II).

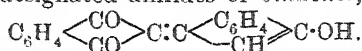
A deep red solution containing the acetate of a dianil is obtained if indandione is heated with aniline (20 parts) and glacial acetic acid (5 parts). When this is mixed with dilute acetic acid and poured into brine, the hydrochloride is precipitated, and from this the free base is obtained by treatment with dilute sodium hydroxide. *Indandione dianil*, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{NPh}) \diagdown \\ \diagdown \text{C}(\text{NPh}) \diagup \end{array} \text{CH}_2 \cdot \text{H}_2\text{O}$, crystallises in brownish-red, stout prisms, m. p. 180—181°, loses water at 100°, and then has m. p. 176—177°. The *hydrochloride*, $\text{B} \cdot \text{HCl} \cdot \text{H}_2\text{O}$, forms dark red, glistening prisms, which sinter at 253—260°; the anhydrous salt is somewhat paler in colour. Two *sulphates* are described: $\text{B}_2 \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, dark red, rhombic crystals, and $\text{B} \cdot \text{H}_2\text{SO}_4$, microscopic, red needles. The *diacetate* is also dark red, and is quickly hydrolysed by water.

These anils are completely hydrolysed to indandione and aniline by warming with excess of dilute hydrochloric acid. With certain quantities of acid, however (1HCl to 2 mols. of the monoanil or 3HCl to 2 mols. of the dianil), the blue anil of bindone is formed (Liebermann, *A.*, 1898, i, 200, and following abstract). The diacetate of the above dianil is produced, on the other hand, when bindone is warmed with aniline (6 parts) and glacial acetic acid (1 part) for some time, thus:

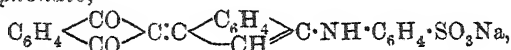


J. C. W.

Indandione and Bindone. II. Action of Aromatic Amines on Bindone. WILHELM WISLICENUS and HERMANN SCHNECK (*Ber.*, 1917, 50, 189—198).—The production of blue colouring matters from bindone by the action of amines was briefly described by Liebermann (*A.*, 1898, i, 200). Contrary to the original statement, it is found that methyl- and ethyl-anilines behave like primary bases. No amines react, however, which are too feebly basic to bring about the enolisation of bindone, and it is usually noticed that before the blue colour appears there is a stage which represents the violet-red salts of the enol. The blue compounds are consequently designated anilides of *bindenol*,



Bindenylaniline, $\text{C}_{24}\text{H}_{15}\text{O}_5\text{N}\cdot\text{H}_2\text{O}$, crystallises in bundles of dark blue, filamentous needles, m. p. 224—225°, and forms a *dihydrochloride*, B_2HCl , in olive-green, elongated leaflets. Bindone does not react with sulphanilic acid in glacial acetic acid unless sodium acetate is added, and then it forms *sodium p-bindenylamino-benzenesulphonate*,



in tufts of deep blue filaments, decomp. above 230°.

Bindenylethylaniline, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{C}:\text{C} \begin{array}{c} \diagdown \text{C}_6\text{H}_4 \\ \diagup \text{CH} \end{array} \text{C}:\text{NEtPh}$, crystallises in blackish-blue prisms, m. p. 181—182°, and forms a *monohydrochloride*, matted needles, and a *dihydrochloride*, greenish-yellow, elongated, six-sided tablets.

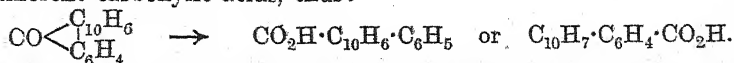
Dimethyl- and diethyl-aniline merely enolise bindone under the above conditions, but condensation of another kind takes place under the influence of zinc chloride. *p-Bindenylphenyldimethylamine*, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{C}:\text{C} \begin{array}{c} \diagdown \text{C}_6\text{H}_4 \\ \diagup \text{CH} \end{array} \text{C}:\text{C}_6\text{H}_4\cdot\text{NMe}_2$, may be isolated from the dark green fusion obtained in this way in the form of irregular, green leaflets, m. p. 234—235°. Diphenylamine also gives a green fusion, and does not behave like the above secondary anilines.

J. C. W.

3:4-Benzofluorenone. ALFRED SCHAARSCHMIDT (*Ber.*, 1917, 50, 293—294. Compare Pfeiffer, this vol., i, 145).—The ketone which Pfeiffer described in 1907 must have been the metastable form of 3:4-benzofluorenone, or a different compound altogether.

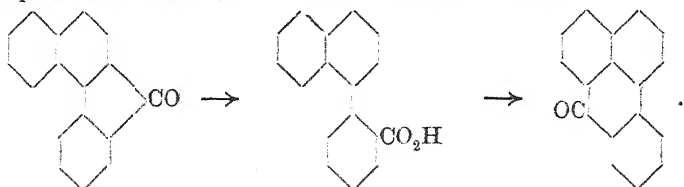
J. C. W.

A New Benzanthrone Synthesis. ALFRED SCHAARSCHMIDT [with EUGEN GEORGEACOPOL] (*Ber.*, 1917, 50, 294—303).—When 3:4-benzofluorenone is fused with potassium hydroxide, the ring bearing the ketone group can be ruptured in two ways, giving different carboxylic acids, thus:



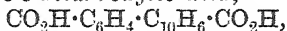
If these acids were dissolved in concentrated sulphuric acid, the phenylnaphthoic acid could only give the original ketone again,

whereas the naphthyl residue in the naphthylbenzoic acid might perhaps rotate, and so give rise to benzanthrone, thus:

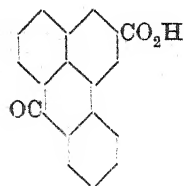


The fact that the sulphuric acid solution is fluorescent shows that benzanthrone is indeed formed. The reaction represents a new synthesis of benzanthrone, and has therefore been extended to derivatives of 3:4-benzofluorenone. In the case of the 1-carboxy- and 1-benzoyl-derivatives, it is found that the rupture of the link between the carbonyl group and the naphthalene ring and the subsequent condensation to benzanthrone are operations which proceed almost quantitatively.

3:4-Benzofluorenone-1-carboxylic acid (A., 1916, i, 47) is heated with potassium hydroxide at 230—235°, and so converted into 1-phenylnaphthalene-o-3-dicarboxylic acid,



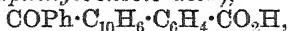
which forms glistening crystals, m. p. 288°. This is transformed into benzanthronecarboxylic acid (annexed formula), bright yellow



needles, m. p. 347°, by dissolving it in concentrated sulphuric acid or by converting it into the chloride by means of phosphorus pentachloride, warming this with aluminium chloride in carbon disulphide, and boiling the acid chloride so formed with dilute potassium hydroxide. Benzoylbenzanthrone, slender, pale yellowish-green needles, m. p. 206°, is obtained by condensing the chloride of either the above

mono- or di-carboxylic acid with benzene by the agency of aluminium chloride.

1-Benzoyl-3:4-benzofluorenone may also be converted by alkaline fusion into 3-benzoyl-1-phenylnaphthalene-o-carboxylic acid (o-3-benzoyl- α -naphthylbenzoic acid),



m. p. 280—282°.

1-Phenylnaphthalene-o-3-dicarboxylic acid forms a bromo-compound, slender, yellowish-grey crystals, m. p. 282°, which may be condensed to bromobenzoylbenzanthrone, yellowish-green crystals, m. p. 242°.

With the formation of benzanthronecarboxylic acid, there is no possibility of further intramolecular condensations, but two molecules of this acid may unite through the naphthalene residues. A small quantity of a very powerful violet dye, which is most probably a compound of such a type, is formed during the alkaline fusion. The production of this dye in quantity and its characteristics will be described later.

J. C. W.

Chrysarobin. III. O. HESSE (*Annalen*, 1917, 413, 350—378. Compare A., 1912, i, 277).—The first part of the paper deals with a re-examination of the constituents of commercial chrysarobin and with the behaviour towards hydriodic acid of its mixtures with chrysophanic acid and emodin methyl ether. The work was undertaken in consequence of Tutin and Clewer's description of the constituents of commercial chrysarobin (P., 1913, 20, 285), in particular, of dehydroemodinanthranol monomethyl ether. Tutin and Clewer assert that the author overlooked this, because by his method of separation by demethylation by hydrochloric or hydriodic acid it would be converted into emodinol. The author retaliates by asking how hydrochloric acid could effect such a conversion, and by stating that if hydriodic acid effected such a reduction iodine must be liberated, a phenomenon which he and Tutin and Clewer have not observed.

Directions are given for the preparation of pure chrysarobin or chrysarobinum purum, by which the author means officinal chrysarobin or chrysarobinum venale freed from anthraquinones and from the constituents insoluble in light petroleum. It consists of chrysophanol and emodinol and their methyl ethers. Chrysarobol is the only crystalline substance which has been isolated from the constituents of commercial chrysarobin insoluble in light petroleum.

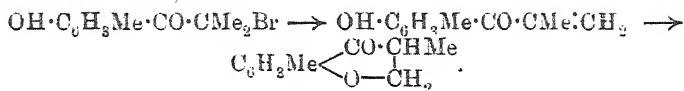
The investigation shows that, although commercial chrysarobins from different sources vary, occasionally considerably, in their composition, chrysophanol, emodinol, and its methyl ether together constitute usually more than 80% of the substance, substances insoluble in light petroleum, chrysophanic acid, emodin and its methyl ether together constitute usually 10% or less, whilst loss and substances not definitely characterised represent about 10%. The presence of ararobinol and dehydroemodinanthranol monomethyl ether has not been detected. C. S.

The Aloins. E. LÉGER (*Ann. Chim.*, 1916, [ix], 6, 318—381).—A résumé of work already published (compare A., 1900, i, 512; 1902, i, 549, 685; ii, 484; 1903, i, 356; 1904, i, 907; 1905, i, 532; 1907, i, 545, 631; 1908, i, 40, 980; 1910, i, 463, 543; 1911, i, 140, 734). W. G.

New Active Principles in the Genus *Xanthoxyllum*. H. BOCQUILLON (*Rép. Pharm.*, 1917, 28, 66; from *Pharm. J.*, 1917, 98, 275).—In continuation of previous work, the occurrence of crystalline neutral principles in different members of the genus *Xanthoxyllum* has been established, and these substances have been shown to be lactones. From *X. caribæum*, light petroleum extracts the lactone, *carixanthide*, $C_{12}H_{14}O$, colourless needles, m. p. 285°. Similarly, *X. carolinianum* yields *carolixanthide*, needles, m. p. 119°. The occurrence in the seeds of *X. piperitum* of the crystalline substance, m. p. 80°, isolated many years ago by Stenhouse (*Annalen*, 1854, 89, 251; 1857, 104, 236), is confirmed, as well as the presence of α -xanthoxylin, colourless plates, m. p. 162°, and β -xanthoxylin, m. p. 187°, in the seeds of *X. octoxyllum*, as

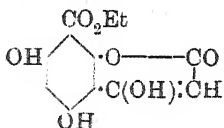
recorded by Leprince (A., 1912, ii, 479). All these substances are accompanied by fixed or volatile oils. H. W.

1 : 1 : 4-Trimethylcoumaranone and 3 : 6-Dimethylchromanone (3 : 6-Dimethyl-1 : 4-benzopyrone). K. VON AUWERS (*Ber.*, 1917, 50, 221—224. Compare A., 1914, i, 1136).—Genuine 1 : 1 : 4-trimethylcoumaranone, b. p. 120°/15 mm., D_4^{20} 1.071, n_D^{20} 1.540, semicarbazone, m. p. 202—203°, has now been obtained by methylating 1 : 4-dimethylcoumaranone by means of methyl iodide and sodamide. The compound, which was obtained by the action of diethylaniline on *m*- α -bromoisobutyryl-*p*-cresol, can also be prepared by warming an aqueous-alcoholic solution of *m*- β -chloroisobutyryl-*p*-cresol with sodium carbonate. It therefore has the alternative structure of 3 : 6-dimethyl-1 : 4-benzopyrone, and its formation by the older method involves the production of an unsaturated ketone, thus :



J. C. W.

Preparation of Benzylidene Compounds of Ethyl 4 : 5 : 7-Trihydroxycoumarin-8-(or 6)-carboxylate. ADOLF SONN (*Ber.*, 1917, 50, 138—144).—Leuchs and Sperling have shown (A., 1915, i, 141) that the "lactone" which Jerdan obtained from ethyl acetonedicarboxylate (T., 1897, 71, 1111) is in all probability a hydroxycoumarin derivative of the annexed formula. As a "benzotetronic acid" it should therefore condense very readily



with aldehydes (compare Anschütz, A., 1909, i, 660), and this is found to be the case. The following 3-benzylidene derivatives were obtained by merely mixing hot alcoholic solutions of the ester and aldehyde and cooling the liquid; *anisylidene*-, a mass of fibrous, orange-yellow needles, m. p. 208°; *p*-hydroxybenzylidene-, m. p. 194—195°; *salicylidene*-, almost colourless tufts, m. p. 180°; *vanillylidene*-, orange-red sheaves, m. p. 247°; *piperynylidene*-, orange-yellow tufts, m. p. 200°; *o*-*p*-dihydroxybenzylidene-, brownish-yellow, granular aggregates of prisms, decomp. above 200°. The first two were reduced by means of zinc dust and glacial acetic acid to the 3- β -*p*-methoxyphenylethyl- (elongated, colourless tablets, m. p. 235°) and 3- β -*p*-hydroxyphenylethyl-derivatives (colourless plates, m. p. 215°) respectively. J. C. W.

Thiophen Series. VIII. Some Derivatives of 2-Aceto-thienone. WILHELM STEINKOFF and DORA JAFFÉ (*Annalen*, 1917, 413, 333—342).—Contrary to experience in the benzene series the simultaneous production of two isomerides in the thiophen series has been very seldom observed.

The nitration of 2-acetothienone, first done by Meyer and Peter in 1884—1885, is effected with much better results by adding slowly

a solution of nitric acid, D 1.52, in acetic anhydride to a solution of 2-acetothienone in the same solvent cooled in a freezing mixture, the temperature being kept below -6° during the addition. The two nitro-2-acetothienones produced have m. p. $88-89^{\circ}$ and 127° respectively (not 86° and 122.5° , as recorded in the literature). Attempts to discover a more convenient method of separating the two isomerides have been unsuccessful, and the orientation of the nitro-groups has not yet been settled owing to experimental difficulties.

The nitro-2-acetothienone, m. p. 88° , is reduced by tin and warm concentrated hydrochloric acid to the stannichloride of amino-2-acetothienone, $2\text{COMe}\cdot\text{C}_4\text{H}_2\text{S}\cdot\text{NH}_2\cdot\text{H}_2\text{SnCl}_6$, brownish-orange crystals, m. p. $202-203^{\circ}$ (decomp.), from which the acetylaminio-2-acetothienone, $\text{NHAc}\cdot\text{C}_4\text{H}_2\text{S}\cdot\text{COMe}$, brown crystals, m. p. $270-271^{\circ}$, can be obtained.

The nitro-2-acetothienone, m. p. 127° , forms an oxime, $\text{NO}_2\cdot\text{C}_4\text{H}_2\text{S}\cdot\text{COMe}\cdot\text{NOH}$, crystals, m. p. 127° , but the isomeride of lower m. p. yields a mixture of several substances under the same conditions. Attempts to apply the Beckmann transformation have been unsuccessful.

2-Acetothienone forms a semicarbazone, leaflets, m. p. $190-191^{\circ}$, benzoylhydrazone, colourless crystals, m. p. $187-188^{\circ}$, p-nitrophenylhydrazone, stout, dark red crystals, m. p. $181-182^{\circ}$, aminoguanidino-derivative, $\text{C}_4\text{H}_2\text{S}\cdot\text{COMe}\cdot\text{N}\cdot\text{NH}\cdot\text{C}(\text{NH}_2)_2\cdot\text{NH}$, small needles, m. p. $83-83.5^{\circ}$ (picrate, $\text{C}_7\text{H}_{10}\text{N}_4\text{S}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, yellow crystals, decomp. $247-248^{\circ}$, with previous sintering and darkening), and the condensation derivative with p-phenetidine, $\text{C}_4\text{H}_2\text{S}\cdot\text{COMe}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, brownish-golden-yellow needles, m. p. $90.5-91^{\circ}$.

2-Acetothienoneoxime reacts with chloral in the smallest possible quantity of cold benzene to form chloral-2-acetothienoneoxime, $\text{C}_4\text{H}_2\text{S}\cdot\text{COMe}\cdot\text{N}\cdot\text{O}\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$, colourless crystals, m. p. 87° .

C. S.

Thiophen Series. IX. New Method of Preparation of Thienyl Ketones. WILHELM STEINKOPF (*Annalen*, 1917, 413, 343-349).—Lecher's method (A., 1913, i, 1166) of preparing ketones of the benzene series is found to be even more effective in the thiophen series; acid chlorides of the aliphatic or of the aromatic series may be employed, and hydrogen chloride is evolved at a lower temperature, so that the reaction can be effected in open vessels.

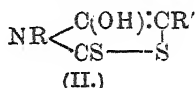
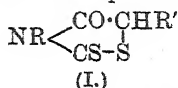
Some light is thrown on the catalytic activity of the phosphoric oxide by the discovery that acid anhydrides can replace acid chlorides. Hydrogen chloride, therefore, is not essential to the catalysis. When an acid anhydride is used, the reaction proceeds, in the author's opinion, with the intermediate formation of an acyl-metaphosphoric acid (compare acetylsulphuric acid): (1) $\text{P}_2\text{O}_5 + 2\text{Ac}_2\text{O} = 2\text{PO}_2\cdot\text{OAc}$, (2) $\text{PO}_2\cdot\text{OAc} + \text{C}_4\text{H}_2\text{S} = \text{C}_4\text{H}_2\text{S}\cdot\text{COMe} + \text{PO}_2\cdot\text{OH}$, and (3) $\text{PO}_2\cdot\text{OH} + \text{PO}_2\cdot\text{OAc} = \text{P}_2\text{O}_5 + \text{CH}_3\cdot\text{CO}_2\text{H}$. When an acid chloride is used, equation (1) becomes $\text{P}_2\text{O}_5 + \text{CH}_3\cdot\text{COCl} = \text{PO}_2\cdot\text{OAc} + \text{PO}_2\text{Cl}$, and (3) becomes $\text{PO}_2\cdot\text{OH} + \text{PO}_2\text{Cl} = \text{P}_2\text{O}_5 + \text{HCl}$.

The acetylmetaphosphoric acid seems not to be formed from metaphosphoric acid itself, as the latter cannot be used in place of phosphoric oxide.

By this method thiophen and about 2% of its weight of phosphoric oxide react with acetyl chloride at 98—130° to give 52% of the theoretical yield of 2-acetothienone (the same yield is obtained with acetic anhydride at 140°), with chloroacetyl chloride at 130—140° to give *o*-chloro-2-acetothienone in poor yield, with benzoyl chloride at 120—125° to give phenyl 2-thienyl ketone, and with *o*-toluoyl chloride at 130—140° to give *o*-tolyl 2-thienyl ketone.

Benzene, acetic anhydride, and phosphoric oxide at 100—140° do not yield acetophenone. C. S.

Stereochemistry of Rhodanines. I. STEN KALLENBERG (*Ber.*, 1917, 50, 90—100).—The general characteristics of the group of substances now known as rhodanines have been established chiefly by Andreasch and his co-workers. Among other reactions, it has been shown that condensations with aldehydes at the carbon atom numbered 5 can be readily induced (compare Andreasch, and also Stieger, this vol., i, 171). This fact suggests that rhodanines can behave as thiazolines (II) as well as thiazolidines (I), which, of course, would be expected from analogies. Since carbon atom 5 is



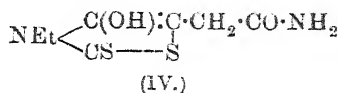
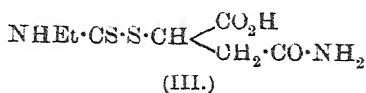
asymmetric in formula (I), but not in (II), it should therefore be possible to decide whether one structure is favoured before the other. To this end the author has applied Holmberg's methods for preparing rhodanines (A., 1910, i, 361) to optically active materials, but he finds that, although the solutions remain active up to the last stage, the isolated rhodanines are always inactive. It appears, therefore, that structure (I) is only transient.

d-Trithiocarbodipropionic acid, $\text{CS}(\text{S} \cdot \text{CHMe} \cdot \text{CO}_2\text{H})_2$, prepared by the resolution of the inactive acid (A., 1905, i, 325), was warmed with aniline and water, but the 3-phenyl-5-methylrhodanine so formed was inactive. It was considered that heating was detrimental, so this method was abandoned.

The alternative method required optically active halogeno-acids. *l*-β-Bromosuccinamic acid, $[\alpha]_D^{15} - 70.03^\circ$, was prepared for this purpose by the interaction of potassium bromide, sodium nitrite, 3*N*-sulphuric acid, and asparagine. Incidentally, *i*-β-iodosuccinamic acid, long prisms, m. p. 118—120°, was prepared from this by the action of an acetone solution of sodium iodide, the racemisation being in accordance with Westerlund's experience (A., 1915, i, 771).

When a solution of potassium ethyldithiocarbamate, prepared by mixing potassium hydroxide, ethylamine, and carbon disulphide, is mixed with *l*-β-bromosuccinamic acid, neutralised with sodium carbonate, and then acidified after some hours, *d*-β-ethyldithiocarbamylsuccinamic acid (III) separates in small leaflets, m. p. 112—113°, $[\alpha]_D + 55.6^\circ$. This readily undergoes dehydration to the rhodanine, for example, when an alkaline solution is left for some

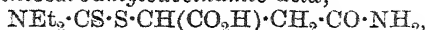
time. 3-Ethylrhodanine-5-acetamide (IV) is a pale yellow, granular mass, m. p. 107—108°, and is optically inactive.



The rhodanine dissolves in dilute sodium hydroxide to give a deep red solution, from which sulphuric acid precipitates inactive β -ethylthiocarbamylsuccinamic acid in colourless leaflets, m. p. 108—109°, which can also be obtained from *i*- β -iodosuccinamic acid as above.

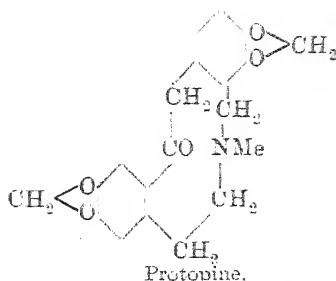
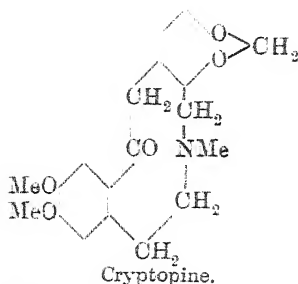
3-Phenylrhodanine-5-acetamide, thin, greenish-yellow tablets, m. p. 171—173°, is formed from either halogenosuccinamic acid, the intermediate hydrate being stable only in the form of its salts.

1- β -Diethylthiocarbamylsuccinamic acid,



is made in the same way, starting from diethylamine. It forms small prisms, m. p. 126—128°, $[\alpha]_D -18.8^\circ$, and yields an ethyl ester, m. p. 85—86°, which is inactive. When the aqueous solution is boiled, with or without acids, it suffers hydrolysis, *i*- β -diethylthiocarbamylsuccinamic acid, m. p. 109—111°, being formed, whilst hydrolysis with alkalis leads to the production of fumaric acid, m. p. 216—218°. On treatment with alkaline permanganate in the cold, one sulphur atom is exchanged for oxygen, *d*- β -diethylthiocarbamylsuccinamic acid, $\text{NEt}_2 \cdot \text{CO} \cdot \text{S} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, being formed, in colourless needles, m. p. 144—145° (decomp.), $[\alpha]_D +74.3^\circ$. Inactive β -diethylthiocarbamylsuccinamic acid, m. p. 131—132° (decomp.), is obtained from β -iodosuccinamic acid, it yields inactive β -diethylthiocarbamylsuccinamic acid, nodules of prisms, m. p. 139—140°. J. C. W.

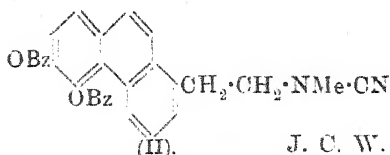
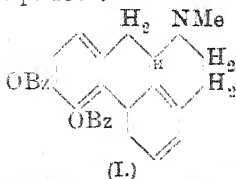
Cryptopine and Protopine. WILLIAM HENRY PERKIN, jun. (T., 1916, 109, 815—1028).—The paper is mainly occupied with the results of an exhaustive and laborious investigation of the degradation and other products of cryptopine with a view to establishing its constitution. The only degradation product obtained previously was *m*-hemipinic acid, showing the presence of a dimethoxybenzene nucleus, but there was strong reason to believe that there was also present a second benzene nucleus to which a methylenedioxy-group was attached. In the present investigation the alkaloid was subjected to the action of a long series of oxidising and hydrolytic agents under a great variety of conditions, but in every case the piperonyl ring was completely destroyed, and the only substances that could be isolated were derived from the dimethoxybenzene nucleus. This difficulty was at length overcome by reducing cryptopine methosulphate with sodium amalgam, when methyltetrahydrocryptopine was formed, and by dehydration with acetyl chloride was converted into anhydromethyltetrahydrocryptopine, from the oxidation products of which piperonyl derivatives could be isolated. Working on this and other lines, many series of derivatives of cryptopine and of the closely related protopine were prepared, and from the results the annexed formulæ were deduced for the two alkaloids:



The evidence brought forward to prove the nature and relative positions of the various groups and rings cannot be recapitulated here; it is summarised by the author in the introduction to the paper (pp. 819-877), to which reference must be made. In the course of the investigation a very large number of new substances were prepared, and detailed descriptions of these and of their relationships will be found in the experimental section of the paper.

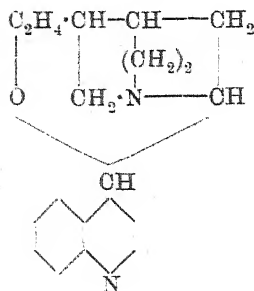
T. H. P.

The Morphine Alkaloids. V. J. VON BRAUN and E. AUST (*Ber.*, 1917, 50, 43-44).—The constitution of *apomorphine* being known, it might be expected to behave differently from morphine towards cyanogen bromide. Instead of losing the *N*-methyl group, it should, in the light of the experience recently gained with hydrogenated *isoquinolines* (this vol., i, 162), suffer rupture of the ring. *Dibenzoylapomorphine* (I) does behave in this way, yielding the compound II as an optically inactive, crystalline powder, m. p. 157°.



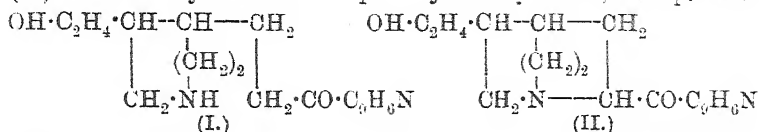
J. C. W.

Cinchona Alkaloids. XVIII. α -isoCinchonine. PAUL RABE and BRUNO BÖTTCHER (*Ber.*, 1917, 50, 127-133).—In his comprehensive survey of the chemistry of the cinchona alkaloids (*A.*, 1906, i, 762) Koenigs suggested that α -isocinchonine is an oxide of the annexed formula. This is now confirmed, but the question whether the C_6H_4 residue is $-CH_2\cdot CH_2-$ or $:CHMe$ is left open. α -isoCinchonine is therefore to be regarded as the internal oxide of a hydroxy-dihydrocinchonine.



α -isoCinchonine is recovered unchanged after boiling with dilute hydrochloric acid for several hours, but with dilute acetic or phosphoric acid, in the dark and in the

absence of air, it is converted into a toxine, *hydroxydihydrocinchonine* (I), which crystallises in rectangular plates, m. p. 125°, $[\alpha]_D^{25} -24.9^\circ$, and forms an amorphous phenylhydrazone and a *picrate*, red prisms, m. p. 220—221° (decomp.). The toxine reacts with sodium hypobromite to form a bromo-imine, which condenses in the presence of sodium ethoxide to *hydroxydihydrocinchoninone* (II). This crystallises in pale yellow needles, m. p. 170°.



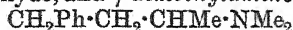
$[\alpha]_D^{15} + 36^\circ$, after one hour, $+69.2^\circ$ (constant) after twenty-two hours, and forms a *picrate*, in many-sided, yellow platelets, m. p. 222—224°.

J. C. W.

Preparation of 2:6-Dimethylpiperidines Substituted in the 2-Position, including their 1-Methyl Derivatives. H. M. JUDD and G. A. R. KON (Brit. Pat., 1916, 103541; from *J. Soc. Chem. Ind.*, 1917, 36, 353).—By using sodium in amyl alcohol instead of sodium or aluminium amalgam for reducing the corresponding 4-piperidones, the resulting piperidine derivative is almost entirely the physiologically active isomeride instead of a mixture of two isomerides. A better yield is obtained and the trouble of isomerising the mixture is avoided. Details are given of the reduction of vinylidacetoneamine (2:2:6-trimethylpiperidone). H. W.

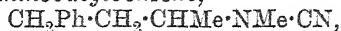
Rupture of the Hydrogenated Indole and Quinoline Rings by Reduction. IV. 2-Methyltetrahydroquinoline. J. von BRAUN and L. NEUMANN (*Ber.*, 1917, 50, 50—55. Compare this vol., i, 167).—It has already been shown that when the quaternary methochloride of dihydroindole is treated with sodium amalgam, rupture of the pyrrole ring between the nitrogen atom and the chain of methylene groups takes place to a certain extent, and that this type of reduction is particularly favoured if there is a methyl group attached to the carbon atom adjacent to the nitrogen atom. In the case of tetrahydroquinoline, however, such a reaction has not yet been observed. Either the ring is ruptured between the nitrogen atom and the benzene nucleus or else one of the *N*-methyl groups is eliminated. It was considered to be worth while, however, to test whether a methyl group in position 2 would be favourable, as in the case of the indole derivatives, but it is found that 2-methyltetrahydroquinoline behaves exactly like tetrahydroquinoline. There appears, therefore, to be a fundamental difference between the indole and quinoline rings in this respect.

2-Methylquinoline is readily converted by successive stages into trimethyltetrahydroquinolinium chloride, and this yields a greater amount of the reduction products than is obtained in the case of tetrahydroquinoline. The mixture consists of 1:2-dimethyltetrahydroquinoline (40%), which is removed as the non-volatile compound with formaldehyde, and γ -dimethylaminobutylbenzene,



(60%), which is volatile in steam. This base is a limpid liquid, b. p. 124—125°/20 mm., which forms a *hydrochloride*, m. p. 127—129°, a flesh-red *platinichloride*, m. p. 173°, a *picrate*, m. p. 113—114°, and a *methiodide*, m. p. 128°.

γ-Cyanomethylaminobutylbenzene,



b. p. 188—189°/24 mm., is formed when the dimethyl base is treated with cyanogen bromide, together with a small amount of the hygroscopic *methobromide* of the dimethyl base, m. p. 142°. When the cyano-compound is heated with hydrochloric acid at 170°, it is hydrolysed to *γ*-methylaminobutylbenzene, which has b. p. 112—114°/14 mm., and yields a *hydrochloride*, m. p. 94—96°, an orange-red *platinichloride*, m. p. 169°, and a *phenylthiocarbamide*, m. p. 103—104°.

When the oily benzoyl derivative of this base is melted with phosphorus pentachloride and then distilled, up to 115° under ordinary pressure, then to 185° under 20 mm., the primary chloride, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{NMe}\cdot\text{CPhCl}_2$, decomposes to a slight extent into methyl chloride and the imino-compound,



but mainly into benzonitrile, methyl chloride, and *γ*-chlorobutylbenzene. When treated with water, the imino-chloride changes into *γ*-benzoylaminobutylbenzene (Harries, A., 1903, i, 815), and the benzonitrile and *γ*-chlorobutylbenzene can then be removed by a current of steam. The nitrile is then separated by hydrolysis with alcoholic hydrochloric acid in the cold, leaving *γ*-chlorobutylbenzene, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHMeCl}$, as a pleasant-smelling oil, b. p. 113—116°/16 mm. This readily yields *α*-methylhydrindene, b. p. 183—185° (not quite pure), when warmed with aluminium chloride and light petroleum, which is an interesting reaction, in view of the fact that the closely related *γ*-chloropropylbenzene does not yield hydrindene (A., 1912, i, 435).

J. C. W.

4. Quinolyl Ketones. III. Synthesis of Substances Related to Quinine. PAUL RABE, RICHARD PASTERNAK, and KARL KINDLER (*Ber.*, 1917, 50, 144—156. Compare A., 1913, i, 513, 514).—The synthesis of some simple 4-quinolyl ketones has already been described. Of the three methods which were tested, the best is the condensation of 4-quinolylcarboxylates with esters, by Claisen's method, followed by ketone hydrolysis. If the 4-quinolylacetic esters or the ketones are treated with bromine, the aliphatic chains are attacked, and the derivatives so formed can then be condensed with amines. The *αβ*-amino-ketones may then be reduced to amino-alcohols, which are more or less related to the cinchona alkaloids, according to the nature of the original quinoline derivative and the amine employed, thus: $\text{Q}\cdot\text{CO}\cdot\text{CH}_2\text{R} \rightarrow \text{Q}\cdot\text{CO}\cdot\text{CHRBr} \rightarrow \text{Q}\cdot\text{CO}\cdot\text{CHR}\cdot\text{N} < \rightarrow \text{Q}\cdot\text{CH}(\text{OH})\cdot\text{CHR}\cdot\text{N} <.$

The synthesis of such amino-alcohols is being rapidly developed, in order, if possible, to decide on what groupings or structure the physiological properties of quinine depend. The closing of the quinuclidine ring is not yet described, but the necessary conditions

will not be difficult to find, a good deal of encouragement having been received already.

Ethyl quinate is condensed with ethyl acetate to form *ethyl 6-methoxy-4-quinoloylacetate*, $\text{OMe} \cdot \text{C}_9\text{H}_5\text{N} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, which crystallises in almost colourless, matted needles, m. p. $84-85^\circ$, gives a *hydrobromide*, yellow crystals, m. p. $159-160^\circ$, and yields 6-methoxy-4-quinolyl methyl ketone, m. p. $89-90^\circ$, on hydrolysis with 25% sulphuric acid (compare Kaufmann, A., 1912, i, 1017). *Ethyl bromo-6-methoxy-4-quinoloylacetate* is obtained by the action of bromine, diluted with chloroform, on the above hydrobromide. It is pale yellow, has m. p. $81-82^\circ$, forms a *hydrobromide*, m. p. 129° , and yields 6-methoxy-4-quinolyl bromomethyl ketone, $\text{OMe} \cdot \text{C}_9\text{H}_5\text{N} \cdot \text{CO} \cdot \text{CH}_2\text{Br}$, on hydrolysis with 24% hydrobromic acid. The free ketone is pale yellow, has m. p. $66-67^\circ$, is not very stable, forms a *hydrobromide*, m. p. $197-198^\circ$, and can also be prepared by brominating 6-methoxy-4-quinolyl methyl ketone. When the hydrobromide is left with piperidine (3 mols.) diluted with benzene, 6-methoxy-4-quinolyl piperidinomethyl ketone is formed as an oil, which gives a *hydrobromide*, 1HBr , m. p. $182-185^\circ$ (decomp.). This ketone, dissolved in concentrated hydrobromic acid, may be reduced by means of hydrogen and palladium-black to α -6-methoxy-4-quinolyl- β -piperidinoethyl alcohol, $\text{C}_5\text{H}_{10}\text{N} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{C}_9\text{H}_5\text{N} \cdot \text{OMe}$, which crystallises in colourless prisms, m. p. 109° .

Ethyl 4-quinoloylacetate (*loc. cit.*) forms a *hydrobromide*, m. p. 162° (decomp.), which can be converted into *ethyl bromo-4-quinoloylacetate*, m. p. $95-96^\circ$ (*hydrobromide*, brilliant yellow, m. p. $127-128^\circ$; *platinichloride*, reddish-yellow, m. p. $122-123^\circ$, decomp.). and then into 4-quinolyl bromomethyl ketone, m. p. $74-75^\circ$ (*hydrobromide*, lemon-yellow, m. p. 220° , decomp.). This reacts with piperidine to form 4-quinolyl piperidinomethyl ketone, which is a viscous, yellow oil; *hydrobromide*, B, HBr , m. p. 178° (decomp.); *platinichloride*, $\text{B, H}_2\text{PtCl}_6$, m. p. 263° (decomp.); *picrate*, $\text{B, 2C}_6\text{H}_5\text{O}_7\text{N}_3$, m. p. $133-134^\circ$ (decomp.).

α -4-Quinolyl- β -piperidinoethyl alcohol, the product of the reduction of the ketone, is also a viscous oil, which forms a pale yellow *platinichloride*, $\text{B, H}_2\text{PtCl}_6$, m. p. 232° (decomp.), and a yellowish-green *dipicrate*, m. p. $172-174^\circ$ (decomp.).

When 4-quinolyl bromomethyl ketone hydrobromide is added to a solution of ethyl cincholeupionate in benzene, dissolution soon takes place, and then *ethyl cincholeupionate hydrobromide*, m. p. 126° , gradually separates, leaving *ethyl 1-4'-quinoloylmethyl-5-ethyl-piperidino-4-acetate* in solution, as a viscous mass. The *platinichloride* of this, $\text{C}_{22}\text{H}_{23}\text{O}_3\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$, is a yellowish-brown powder, m. p. 197° (decomp.), and the *picrolonate*, $\text{B, 2C}_{10}\text{H}_8\text{O}_5\text{N}_4$, forms reddish-brown crystals, m. p. $146-147^\circ$. The corresponding *secondary alcohol*,



is also a viscous oil, and its *picrolonate* is reddish-brown.

The "acetoacetic acid" synthesis can be developed a stage

further in this series by treating the sodium compounds of the quinoloylacetic esters with alkyl iodides. Thus, ethyl 4-quinoloylacetate, sodium methoxide, and methyl iodide react to form ethyl α -4-quinoloylpropionate, which has not been purified, but identified by conversion into 4-quinolyl ethyl ketone (*loc. cit.*). J. C. W.

New Method of Preparing Cyclic Ketones. ALFRED SCHAARSCHMIDT (*Ber.*, 1917, 50, 164—169. Compare A., 1914, i, 732).—Eckert and Halla (A., 1914, i, 994) obtained a compound, which they designated 1:2:6:7-diphthaloylacridone, by condensing 1-aminoanthraquinone-2-carboxylic acid with 2-chloroanthraquinone in the presence of sodium acetate and cuprous chloride. A compound which undoubtedly has this constitution was just previously described by Schaarschmidt (*ibid.*, 732; D.R.-P., 269800), and earlier still in D.R.-P., 192436, but it is not identical with Eckert and Halla's substance. It is suggested that the latter may be a dianthraquinonylamine, for aminoanthraquinonecarboxylic acids tend to lose carbon dioxide on heating (see D.R.-P., 268219; *ibid.*, 184).

The paper deals largely with questions of priority, in which Ullmann and Bincer (A., 1916, i, 483) are concerned. J. C. W.

New Stains for Microscopic Work Derived from Methylene-blue. L. TRIBONDEAU and J. DUBREUIL (*Compt. rend.*, 1917, 164, 551—553).—An account of a simple method for preparing methylene-violet and methylene-azure in a pure state. To a 1% aqueous solution of methylene-blue 5—10% of ammonia is added and the mixture heated on a water-bath, when an abundant precipitate is formed, which is filtered off. The filtrate is evaporated in a flat dish at 37—40°, the dry residue being methylene-violet. The precipitate on the paper and in the flask is left exposed to the air for a day until it is deep blue in colour. It is then extracted with water, filtered, and the filtrate evaporated as above, the product being methylene-azure. W. G.

Theory of the Oxidation of Benzidine in its Significance for Peroxydase Investigations. W. MADELUNG (*Ber.*, 1917, 50, 105—111. Compare Woker, this vol., i, 62).—A criticism of Woker's views on the constitution of the benzidine monohydrochlorides and the oxidation product of benzidine. Attention is re-directed to the author's own communications (A., 1911, i, 323, 411, 678). J. C. W.

Preparation of Ether-like Derivatives of Barbituric Acid. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 295492; from *J. Soc. Chem. Ind.*, 1917, 36, 306).—Aryl- or alkyl-aryloxyalkylmalonic acids or diaryloxyalkylmalonic acids or their derivatives, for example, the corresponding esters, acid chlorides, cyanoacetates, or malononitriles, are converted into barbituric acid derivatives by the usual methods. Alternatively, mono-substituted malonic acid derivatives containing one of the substituent groups above speci-

fied are converted into barbituric acids and the second substituent group is introduced by alkylation of the resulting mono-substituted barbituric acids or of the product at an intermediate stage of the conversion. Such ether-like derivatives, containing at least one aryl residue attached to an oxygen atom, possess strong hypnotic action combined with low toxic effects. Ethylphenoxyethylbarbituric acid, diphenoxyethylbarbituric acid, *C-C*-propyl-*p*-tolylloxyethylbarbituric acid, and *C-C*-benzylphenoxyethylbarbituric acid are described.

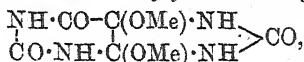
H. W.

[**Derivatives of Uric Acid.**] HEINRICH BILTZ (*Annalen*, 1916, 413, 1—7).—An introduction to the following papers. The results of researches by the author and his co-workers in the uric acid series have now accumulated to such an extent that it seems advisable to give a survey of the region traversed, although the investigations are not yet finished.

C. S.

Derivatives of Uric Acid. HEINRICH BILTZ and MYRON HEYN (*Annalen*, 1916, 413, 7—60).—A series of new reactions of uric acid is described.

The glycol ethers of uric acid itself are more difficult to prepare than are those of many methylated uric acids. 4:5-Dimethoxy-4:5-dihydrouric acid (uric acid-4:5-diglycol dimethyl ether),



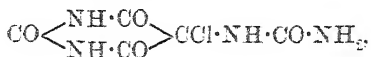
slender needles, m. p. 202—203° (decomp.), is obtained by passing a rapid stream of chlorine into a suspension of uric acid in methyl alcohol, the temperature being kept below 15°; in order to prevent an explosion, the end of the chlorine delivery tube must be about 1 cm. from the bottom of the flask. The corresponding diethyl ether cannot be obtained in a similar manner.

4:5-Dimethoxy-4:5-dihydrouric acid is reduced to uric acid by sodium amalgam and to ψ -uric acid by hydriodic acid, D 1.96, on the water-bath. When boiled with methyl alcohol saturated with hydrogen chloride, it is converted into a substance, $\text{C}_6\text{H}_5\text{O}_5\text{N}_2$, stout prisms with domed ends or tufts of stout needles, m. p. 135—137°, which is regarded as methyl 5-methoxyhydantoin-5-carboxylate, $\begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{CO}\cdot\text{NH} \end{array} > \text{C}(\text{OMe})\cdot\text{CO}_2\text{Me}$, since it is easily reduced to hydantoin by concentrated hydriodic acid and phosphonium iodide on the water-bath.

4:5-Dimethoxy-4:5-dihydrouric acid is converted into alloxantin by 20% hydrochloric acid on the water-bath, but when dissolved in concentrated hydrochloric acid at the ordinary temperature it yields 5-methoxy- ψ -uric acid, $\text{CO} < \begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} > \text{C}(\text{OMe})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, stout rhombohedra, m. p. 202—204° (decomp.). The latter is proved to be a derivative of ψ -uric acid by its reduction to ψ -uric acid by sodium amalgam or hydriodic acid and by its formation from ψ -uric acid, methyl alcohol, and chlorine. By boiling with glacial acetic acid for one hour it is converted into 4-hydroxy-5-methoxy-

4:5-dihydrouric acid, stout prisms, m. p. 202—203° (decomp.), which is reduced to hydantoin by hydriodic acid. The conversion of 4:5-dimethoxy-4:5-dihydrouric acid into ψ -uric acid by hydriodic acid is readily explicable in view of the preceding formation of 5-methoxy- ψ -uric acid.

A solution of uric acid in boiling chloroform or in glacial acetic acid is not attacked by chlorine. When, however, water is present in the latter solvent, reaction occurs; with 5 mols. of water the product is alloxan, whilst with 1 mol. of water, the temperature being kept at about 10°, 5-chloro- ψ -uric acid,



is formed. This substance, m. p. about 125° (decomp.), forms very thin, felted fibres or needles containing 1 mol. $\text{C}_2\text{H}_4\text{O}_2$, which cannot be removed. It is also formed by the action of chlorine on ψ -uric acid dissolved in glacial acetic acid. It is reduced to ψ -uric acid by a concentrated solution of hydrogen iodide in glacial acetic acid on the water-bath, by a solution of potassium iodide, iodine being liberated, or by stannous chloride and hydrochloric acid. Since the last method of reduction proceeds very readily, a very convenient method of converting uric acid into ψ -uric acid is presented by chlorinating a solution of uric acid and 1 mol. of water in glacial acetic acid, removing the dissolved chlorine by a current of dry air at 0°, and treating the solution with stannous chloride and concentrated hydrochloric acid.

By treatment with hot methyl alcohol 5-chloro- ψ -uric acid is converted into 5-methoxy- ψ -uric acid. 5-Ethoxy- ψ -uric acid, $\text{C}_7\text{H}_{10}\text{O}_5\text{N}_4$, forms stout prisms, m. p. 227—228° (decomp.).

Whilst all chloro- ψ -uric acids hitherto known react with water to form the glycols of the corresponding uric acids or their products of decomposition, 5-chloro- ψ -uric acid is unique in yielding 5-hydroxy- ψ -uric acid, $\text{C}_5\text{H}_6\text{O}_5\text{N}_4$, microscopic leaflets, m. p. about 210° (decomp.), which is converted into alloxan and carbamide by boiling water, yields 4:5-dihydroxy-4:5-dihydrouric acid by slow evaporation with water at 45—50° or by treatment with aqueous bromine at the ordinary temperature, and is reduced to ψ -uric acid by hydriodic acid, D 1.96, sodium amalgam, or acidified aqueous potassium iodide. When boiled with methyl or ethyl alcohol, 5-hydroxy- ψ -uric acid is converted into the corresponding 5-alkyloxy- ψ -uric acid; propyl-, benzyl-, and phenyl-oxy-compounds are not produced in a similar manner, and an acetyl derivative cannot be obtained.

When the basic reagent is added only in slight excess, 5-hydroxy- ψ -uric acid intimately mixed with water reacts with aqueous ammonia at 0° and with 33% methylamine, 33% ethylamine, dimethylamine, diethylamine, and aniline at the ordinary temperature to form the following compounds: 5-amino- ψ -uric acid, $\text{C}_5\text{H}_7\text{O}_4\text{N}_5$, H_2O , rectangular or quadratic plates, m. p. 145—147° (decomp.); 5-methylamino- ψ -uric acid, $\text{C}_6\text{H}_9\text{O}_4\text{N}_5$, stout, six-sided or rhombic plates, m. p. 191—192° (decomp.); 5-ethylamino- ψ -uric

acid, stout plates, m. p. 170—171° (decomp.); 5-dimethylamino- ψ -uric acid, stout needles, m. p. 191—192° (decomp.); 5-diethylamino- ψ -uric acid, stout, many-faced crystals (? scalenohedra), m. p. 163—165° (decomp.); and 5-anilino- ψ -uric acid, six-sided leaflets, m. p. 194—196° (decomp.).

5-Amino- ψ -uric acid forms an ammonium salt, $C_5H_7O_4N_5.NH_3$, elongated, flattened rhombs, m. p. 90—95° (decomp.; reddening at about 70°), and a hydrochloride, $C_5H_9O_4N_5.HCl$, microscopic spindles, is reduced to uramil by hydriodic acid, D 1.5, or stannous chloride and hydrochloric acid, and dissolves in 5% aqueous ammonia to yield, after acidification with acetic acid, 5-amino-4-hydroxy-4:5-dihydrouric acid, $C_5H_7O_4N_5$, six-sided plates, m. p. 189—191° (decomp.); attempts to effect a similar ring closure in the preceding 5-alkylamino- ψ -uric acids have been unsuccessful.

spiro-5:5-Hydantoin, $\begin{array}{c} NH \cdot CO \\ | \\ CO \cdot NH \end{array} > C < \begin{array}{c} NH \cdot CO \\ | \\ CO \cdot NH \end{array}$, stout rhombohedra blackening above 400°, prepared by boiling 5-amino-4-hydroxy-4:5-dihydrouric acid with concentrated hydrochloric, nitric, or hydriodic acid, is the parent substance of hypoxanthine (1:7:9-trimethylspiro-5:5-hydantoin) and 1:3:7:9-tetramethylspiro-5:5-hydantoin (Biltz and Krebs, A., 1911, i, 240). It is remarkably stable to acids and is not attacked by alkaline permanganate, but is converted into allantoin by hot, concentrated aqueous barium hydroxide and into potassium uroxyanate by hot aqueous potassium hydroxide, allantoin-5-carboxylic acid being a probable intermediate product in each case.

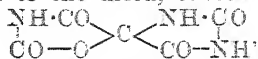
The preceding 5-alkylamino- or -dialkylamino- ψ -uric acids are reduced to 7-alkyl- or 7:7-dialkyl-uramils by hydriodic acid or stannous chloride and hydrochloric acid. This not only proves the position of the substituted amino-group, but also indicates a very convenient method of preparing substituted uramils, particularly 7:7-dimethyluramil. A mixture of pure 5-hydroxy- ψ -uric acid and anhydrous alcohol is shaken vigorously with 33% aqueous methylamine (slightly more than 2 mols.) and the resulting methylammonium salt of 5-methylamino- ψ -uric acid, $C_6H_9O_4N_5.NH_2Me$, stout, badly formed crystals, m. p. 110—115° (decomp.), is boiled with a solution of stannous chloride in concentrated hydrochloric acid, whereby 7-methyluramil is obtained after dilution with dilute hydrochloric acid. 7-Ethyluramil is obtained in a similar manner from the ethylammonium salt of 5-ethylamino- ψ -uric acid, $C_7H_{11}O_4N_5.NH_2Et$, rectangular plates, decomp. about 140—145°. 7:7-Dimethyluramil, $C_8H_{13}O_4N_5.2H_2O$, forms very slender, elongated needles, m. p. 283—285° (decomp.), and in contrast to other uramils is remarkably easily soluble in water.

By reduction with sodium amalgam, 5-amino- and -monoalkylamino- ψ -uric acids yield the corresponding uramils, whilst the 5-dialkylamino- ψ -uric acids yield ψ -uric acid.

Carbamide alloxanate (Behrend and Zieger, A., 1915, i, 165) is obtained by warming a solution of 4:5-dihydroxy-4:5-dihydrouric acid hemihydrate in water containing a little hydrochloric acid at 60—70°.

After many unsuccessful attempts to convert 4:5-dihydroxy-4:5-

dihydrouric acid into caffolide, the following simple method yielded the desired product. The glycol is treated with 20% aqueous potassium hydroxide, and the solution after five minutes is acidified with 30% sulphuric acid at 0°, filtered, and repeatedly extracted with ether; the addition of light petroleum to the dried, concentrated ethereal extracts yields *caffolide*,



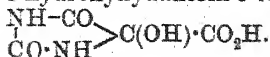
tufts of colourless needles, decomp. 220°. Its *disilver* salt, $\text{C}_5\text{HO}_5\text{N}_2\text{Ag}_2$, needles, is stable to light, and is converted into *isocapocaffeine* (Biltz, A., 1913, i, 1376) by methyl iodide at 100°.

Although methylated caffolides are easily converted into the corresponding 5-hydroxyhydantoin-5-carboxyamides by boiling and evaporating their aqueous solutions, caffolide itself must be boiled with water and the solution evaporated under increased pressure. 5-Hydroxyhydantoin-5-carboxyamide, $\text{C}_4\text{H}_5\text{O}_4\text{N}_2$, forms rectangular plates, m. p. 191° (decomp.), and yields hydantoin by reduction with hydriodic acid and parabanic acid by oxidation with potassium dichromate and sulphuric acid. C. S.

Preparation of Alloxan. HEINRICH BILTZ and MYRON HEYN (*Annalen*, 1916, 413, 60—67).—Finely powdered uric acid is boiled with glacial acetic acid and water (about 5 mols. of the latter), while with continuous, vigorous shaking of the flask a stormy current of chlorine is passed in by a tube reaching almost to the bottom. Towards the end of the reaction the mixture becomes yellowish-green through the presence of dissolved chlorine, and soon after, the uric acid having all dissolved, alloxan monohydrate begins to separate in stout, heavy crystals, the separation being completed by cooling in water at 0°. Unnecessarily prolonged chlorination is to be avoided. The method is recommended as a lecture experiment.

A description is given of the appearance under the microscope of the crystals obtained when the following uric acids (0.03—0.05 gram) are dissolved in concentrated sulphuric acid (about 8 drops) at 40—50° and the clear solutions are stirred into about 5 c.c. of water: uric acid, 1-, 3-, and 7-methyluric acids, 1:3-, 1:7-, 3:9-, and 3:7-dimethyluric acids, 1:3:7-trimethyluric acid, and tetramethyluric acid. C. S.

Alloxanic Acid. HEINRICH BILTZ, MYRON HEYN, and MARGARETE BERGIUS (*Annalen*, 1916, 413, 68—77).—The constitution $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ for alloxanic acid appears never to have been proved and never to have been doubted. Several observations recorded in the literature, such as the oxidation by nitric acid of alloxanic acid to parabanic acid by Schlieper, and its reduction by hydriodic acid to hydantoin by Baeyer, not being readily explicable by the open-chain formula, the authors have investigated the subject, and have proved that alloxanic acid is the cyclic compound, 5-hydroxyhydantoin-5-carboxylic acid,

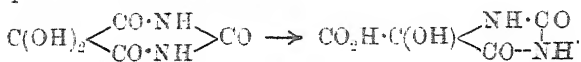


It is shown that the oxidation to parabanic acid proceeds quantitatively. According to the new formula, alloxanic acid is dibasic (compare Limpricht, *Annalen*, 1859, 111, 133), the hydrogen of the carboxyl group and that of the imino-group in position 3 being replaceable by metals. *Methyl alloxanate*, $C_3H_6O_4N_2$, prepared from alloxanic acid and methyl-alcoholic hydrogen chloride in the complete absence of moisture, forms small, pointed, flattened needles, m. p. 171° ; the *ethyl* ester has m. p. 115° . When heated with methyl-alcoholic hydrogen chloride at 100° , the methyl ester is converted into methyl 5-methoxyhydantoin-5-carboxylate (Biltz and Heyn, preceding abstract).

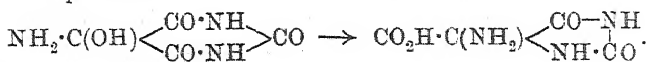
Of the two formulæ of alloxanic acid in question, only the open-chain one contains a carbonyl group attached to two carbon atoms. Such carbonyl groups react normally with hydroxylamine, phenylhydrazine, and semicarbazide, whereas a carbonyl group attached to carbon and to nitrogen does not. It is found that alloxan yields precipitates with the three reagents, whereas the alloxanic ester and 3-methylhydantoin do not, the evidence being thus in favour of the cyclic constitution of alloxanic acid. The hydroxyl group in the latter, however, cannot be detected by phenylcarbimide.

Further support of the cyclic structure is given by the formation of *spiro*-5:5-hydantoin when a mixture of carbamide and methyl alloxanate or methyl 5-methoxyhydantoin-5-carboxylate is heated at 150° in a current of hydrogen chloride.

The formation of alloxanic acid from alloxan is attributed to a kind of pinacolin transformation:



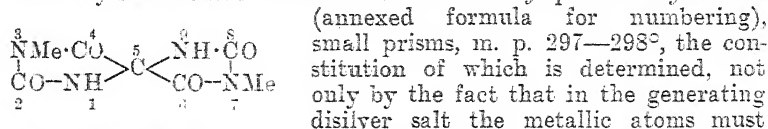
Piloty and Finckh (A., 1904, 1, 824) regard oxonic acid as 5-aminohydantoin-5-carboxylic acid; its formation by the oxidation of uramil is explicable by a transformation of an intermediate oxidation product:



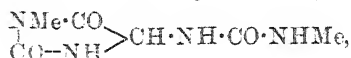
C. S.

***spiro*Hydantoins.** HEINRICH BILTZ, MYRON HEYN, and MARGARETE BERGIUS (*Annalen*, 1916, 413, 77—87).—Since tetramethyluric acid and 1:3:7-trimethyluric acid glycol ether are converted respectively into tetramethyl- and trimethyl-*spiro*-5:5-hydantoin (A., 1911, 1, 240), doubtless by a kind of pinacolin transformation of the intermediate, unstable glycols, which cannot be isolated, it becomes of interest to ascertain whether the more stable uric acid glycols undergo such a transformation. *spiro*-5:5-Hydantoin is obtained by heating 4:5-dihydroxy-4:5-dihydrouric acid with concentrated sulphuric acid on the water-bath, and pouring the cold solution into water. A better yield is obtained by heating the glycol and carbamide at 150° in a current of hydrogen chloride.

The latter is the most convenient method of preparing *spiro-5:5*-hydantoin, alloxan being used in place of the uric acid glycol. The 3:7-*disilver* salt, $C_5H_2O_4N_4Ag_2 \cdot 2H_2O$, crystals, obtained by adding a solution of *spiro-5:5*-hydantoin in aqueous ammonia to a solution of silver nitrate, is converted by methyl iodide and a little dry silver oxide at 100° into 3:7-*dimethylspiro-5:5-hydantoin*

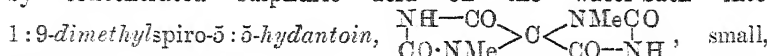


have replaced the acidic hydrogen atoms of the imino-groups between each pair of carbonyl groups in *spiro-5:5*-hydantoin, but also by its conversion in aqueous solution by basic lead acetate on the water-bath into 3:8-*dimethylallantoin*,



stout, indistinctly formed prisms, m. p. 222° (decomp.), from which 3-methylhydantoin is obtained by reduction with hydriodic acid.

4:5-Dihydroxy-3:7-dimethyl-4:5-dihydricuric acid is converted by concentrated sulphuric acid on the water-bath into



four-sided pointed prisms, m. p. $264-265^\circ$, which yields 1:6-*dimethylallantoin*, $C_6H_{10}O_3N_4$, flat, pointed needles, m. p. $226-227^\circ$ (decomp.), by treatment with basic lead acetate, forms the *disilver* salt, $C_7H_6O_4N_4Ag_2$, and is converted into tetramethyl-*spiro-5:5*-hydantoin by shaking with methyl sulphate and aqueous sodium hydroxide. 1:6-Dimethylallantoin is converted into 1-methylhydantoin by reduction with hydriodic acid.

The glycols of 9-methyluric acid and 1:3-dimethyluric acid could not be converted into *spirohydantoin*s. C. S.

Derivatives of 9-Methyluric Acid. HEINRICH BILTZ and MYRON HEYN (*Annalen*, 1916, 413, 87-98).—9-Methyluric acid has hitherto been obtained only with difficulty. The authors prepare it easily from 5-chloro-9-methyl- ψ -uric acid, which is itself obtained as follows. The crude methyluric acid (or mixture), prepared by acidifying the hot solution obtained by heating uric acid, dilute aqueous potassium hydroxide, and methyl iodide in a closed bottle in a water-bath, is finely powdered, mixed with glacial acetic acid, and treated at 0° with a vigorous stream of chlorine, the temperature being kept below 10° . 5-Chloro-9-methyl- ψ -uric acid, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{array} \text{CCl} \cdot \text{NH} \cdot \text{CO} \cdot \text{NHMe}$, leaflets, containing

$\frac{1}{2}C_2H_4O_2$, m. p. $208-210^\circ$ (decomp.), thus obtained, is converted into 4:5-dihydroxy-9-methyl-4:5-dihydricuric acid by luke-warm water, and into 5-methoxy-9-methyl- ψ -uric acid, $C_7H_{10}O_5N_4$, octagonal or quadratic plates, m. p. $195-196^\circ$ (decomp.), and

5-ethoxy-9-methyl-ψ-uric acid, colourless needles, m. p. 222° (decomp.), by rubbing with methyl and ethyl alcohol respectively. By crystallisation from water, the last two compounds are converted into *4-hydroxy-5-methoxy-9-methyl-4:5-dihydrouric acid*, $(C_7H_{10}O_5N_4)$, cubes or rhombohedra, m. p. 170—172° (which yields 3-methylhydantoin by reduction with hydriodic acid), and *4-hydroxy-5-ethoxy-9-methyl-4:5-dihydrouric acid*, thin leaflets, m. p. 190—192°.

9-Methyl-ψ-uric acid, $CO < \begin{smallmatrix} NH \cdot CO \\ NH \cdot CO \end{smallmatrix} > CH \cdot NH \cdot CO \cdot NHMe$, m. p. 260—261° (decomp.), needles or prisms containing $1H_2O$, is obtained by reducing 5-chloro-9-methyl-ψ-uric acid with stannous chloride and concentrated hydrochloric acid, or the 5-alkyloxy-9-methyl-ψ-uric acids at 40—50° with a saturated solution of hydrogen iodide in glacial acetic acid. It is converted by prolonged evaporation with 20% hydrochloric acid into 9-methyluric acid, the identity of which was proved by its m. p., very sparing solubility in boiling water (1 part in 1830), and conversion into 1-methylallantoin, alloxantin, and dialuric acid. By treatment with chlorine, 9-methyluric acid dissolved in glacial acetic acid and a little water is converted into 5-chloro-9-methyl-ψ-uric acid, and from the yield obtained it was calculated that the original crude mixture contained 20—30% of 9-methyluric acid. C. S.

α-, ζ- and δ-Methyluric Acids. HEINRICH BILTZ and MYRON HEYN (*Annalen*, 1916, **413**, 98—124).—The authors have solved the mystery of the three isomeric methyluric acids, for which only one formula is available, namely, Hill's α-methyluric acid, von Loeben's δ-methyluric acid, and Fischer and Ach's ζ-methyluric acid, in all of which, so far as our knowledge goes, the methyl group is in position 3.

α-Methyluric acid was prepared according to Grohmann's directions (A., 1911, i, 691), and purified through the sodium salt in order to remove unchanged uric acid, none of which, however, was found to be present (compare Grohmann, *loc. cit.*). In the purification, about one-half of the sodium salt separates as a solid and the other half remains in solution. The α-methyluric acids obtained from these two portions were separately treated with chlorine and glacial acetic acid (compare preceding abstract), and from the amounts of 5-chloro-9-methyl-ψ-uric acid obtained it was calculated that the α-methyluric acid obtained from the precipitated sodium salt contained about 20%, and that from the soluble sodium salt about 32%, of 9-methyluric acid. By the same method of analysis, the crude α-methyluric acid (not purified through the sodium salt) was estimated to contain about 25% of 9-methyluric acid, and this estimate could be, and was, confirmed by the amount of the water of crystallisation, since 9-methyluric acid crystallises anhydrous and 3-methyluric acid with $1H_2O$.

ζ-Methyluric acid, prepared by Fischer and Ach's method, was examined in the same way, and according to the amount of 5-chloro-

9-methyl- ψ -uric acid obtained was estimated to contain about 10% of 9-methyluric acid.

δ -Methyluric acid synthesised by von Loeben's method cannot contain 9-methyluric acid, and therefore did not yield any 5-chloro-9-methyl- ψ -uric acid. This is the true 3-methyluric acid; the α - and the ζ -acids contain, in addition, 25% and 10% respectively of 9-methyluric acid. The presence of 3-methyluric acid in the α - and ζ -acids is proved not only by their conversion into methylalloxan and 1-methylallantoin by oxidation, and into chloro-3-methylxanthine by phosphoryl chloride at 140—150°, but also in the following new way. By chlorination in dry chloroform, 3-methyluric acid yields a very hygroscopic chlorination product, probably the 4:5-dichloride, which is converted by methyl alcohol into 4-hydroxy-5-methoxy-3-methyl-4:5-dihydrouric acid, $C_7H_{10}O_5N_2$, monoclinic prisms [$a:b:c=0.86806:1:0.67908$; $\beta=56^\circ 8'$], m. p. 207° (decomp.). This substance was obtained from α - and from ζ -methyluric acid, thus proving the presence of 3-methyluric acid in these two acids.

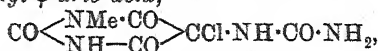
The records state that 1 part of δ -methyluric acid dissolves in 527 parts of boiling water (von Loeben), 1 part of α -methyluric acid in 262 parts (*ibid.*), 1 part of ζ -methyluric acid in about 600, and 1 part of 9-methyluric acid in more than 2000 (Fischer and Ach). These results being peculiar, in view of the compositions ascribed above to the first three acids, the authors have redetermined the solubilities of all the acids in boiling water under the same conditions, and find that mixtures of 9- and 3-methyluric acids are indeed more soluble than either of the constituents. The amount of boiling water required to dissolve 1 part of the acid is: 9-methyluric acid, 1830; 3-methyluric acid, 630; 90% of 3- and 10% of 9-methyluric acids, 360; 70% of 3- and 30% of 9-methyluric acids, 270; ζ -methyluric acid, 475; and α -methyluric acid, 200. The mixtures do not appear to dissolve as isomorphous mixed crystals, but leave a solid phase (or phases) differing in composition and solubility from the portion in solution, so that variable values of the solubility of a given mixture are obtained according to the relative proportions of mixture and water. Uric acid requires 1250 parts, and 3:7-dimethyluric acid 290 parts, of boiling water for solution. All these measurements profess to give only the orders of magnitude, not the accurate values, of the solubility. 7-Methyluric acid exhibits an extraordinary tendency to form supersaturated solutions. C. S.

Derivatives of 1-Methyluric Acid. HEINRICH BILTZ and KARL STRUFE (*Annalen*, 1916, **413**, 124—136).—4:5-Dimethoxy-1-methyl-4:5-dihydrouric acid,
$$\begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C}(\text{OMe}) \cdot \text{NH} \\ \text{CO} \cdot \text{HN} \cdot \text{C}(\text{OMe}) \cdot \text{NH} \end{array} > \text{CO},$$
 six-sided plates, m. p. 225° (decomp.), is obtained by passing a rapid stream of chlorine into a mixture of finely powdered 1-methyluric acid and glacial acetic acid at 0°. The corresponding 4:5-diethoxy-compound forms slender needles, m. p. 212° (decomp.). In

both cases a small amount of the 5-alkyloxy-1-methyl- ψ -uric acid is obtained as a by-product. 5-Methoxy-1-methyl- ψ -uric acid, $\text{CO} \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \text{NH} - \text{CO} \end{smallmatrix} \text{C}(\text{OMe}) \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, rectangular leaflets, m. p. about 192° (decomp.), is obtained (1) when 4:5-dimethoxy-1-methyl-4:5-dihydrouric acid is triturated with concentrated hydrochloric acid or boiled with alcoholic hydrochloric acid, (2) by chlorinating a mixture of 1-methyluric acid or 1-methyl- ψ -uric acid and methyl alcohol at the ordinary temperature. 5-Ethoxy-1-methyl- ψ -uric acid, obtained by similar methods, forms leaflets, m. p. about 216° (decomp.).

4:5-Dimethoxy-1-methyl-4:5-dihydrouric acid is reduced to 1-methyluric acid by 2½% sodium amalgam or by hydriodic acid, D 1.96, on the water-bath, but when hydriodic acid, D 1.5, is used at 60° the product is 1-methyl- ψ -uric acid, which is also obtained in a similar way from 5-methoxy-1-methyl- ψ -uric acid.

5-Chloro-1-methyl- ψ -uric acid,



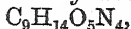
indistinct crystals containing $1\text{C}_2\text{H}_4\text{O}_2$, m. p. about 170° (decomp.), is obtained by chlorinating 1-methyluric acid or 1-methyl- ψ -uric acid in the presence of glacial acetic acid. It is converted into 5-methoxy-1-methyl- ψ -uric acid by gently warming with methyl alcohol containing a few drops of glacial acetic acid, yields 1-methyl- ψ -uric acid by heating with glacial acetic acid saturated with hydrogen iodide, and reacts with water to form 4:5-dihydroxy-1-methyl-4:5-dihydrouric acid, $\text{C}_6\text{H}_8\text{O}_5\text{N}_4$, elongated leaflets, m. p. 140° (decomp.).

When 5-methoxy-1-methyl- ψ -uric acid is dissolved in 4*N*-sodium hydroxide and the solution is acidified with concentrated hydrochloric acid, a substance is obtained which is identical with the 4-hydroxy-5-methoxy-3-methyl-4:5-dihydrouric acid prepared by Biltz and Heyn (preceding abstract) from 3-methyluric acid. It is evident that when 5-methoxy-1-methyl- ψ -uric acid undergoes isomerisation, the formation of the glyoxaline ring may result by the union of the carbamido-group with either of the contiguous carbonyl groups. It has not yet been definitely ascertained in which direction the union occurs, so the product of isomerisation may be either 4-hydroxy-5-methoxy-1-methyl-4:5-dihydrouric acid or 4-hydroxy-5-methoxy-3-methyl-4:5-dihydrouric acid, but the latter is the more probable in view of the evidence obtained by Biltz and Damm (following abstract). 4-Hydroxy-5-ethoxy-3(?)-methyl-4:5-dihydrouric acid, obtained by the isomerisation of 5-ethoxy-1-methyl- ψ -uric acid, forms stout prisms, m. p. 203° (decomp.). C. S.

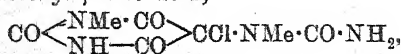
Derivatives of 1:7-Dimethyluric Acid. HEINRICH BILTZ and PAUL DAMM (*Annalen*, 1916, 413, 137—155).—5-Chloro-1:7-dimethyl- $\Delta^{(9)}$ -isouric acid, $\text{NMe} \cdot \text{CO} \cdot \text{CCl} \cdot \text{NMe} \begin{smallmatrix} \text{CO} \\ \text{CO} \cdot \text{NH} - \text{C} = \text{N} \end{smallmatrix}$, obtained by

leading chlorine into a mixture of 1:7-dimethyluric acid and dry chloroform, has m. p. 131° (decomp.), yields 1:7-dimethyluric acid by reduction with hydriodic acid, is converted into apocaffeine by

water, and reacts with methyl and ethyl alcohols to form the glycol ethers; 4:5-dimethoxy-1:7-dimethyl-4:5-dihydrouic acid,



four-sided prisms, m. p. 171° , and the 4:5-diethoxy-compound, $\text{C}_{13}\text{H}_{20}\text{O}_5\text{N}_4$, elongated rhombohedra, m. p. 188 — 189° , which can also be obtained directly from 1:7-dimethyluric acid and the alcohol by means of chlorine. These glycol ethers are reduced to 1:7-dimethyluric acid by hydriodic acid or sodium amalgam, and react with concentrated hydrochloric or sulphuric acid in an interesting manner. The product should be the 4-hydroxy-5-alkyloxy-1:7-dimethyl-4:5-dihydrouic acid by analogy with the behaviour of the glycol ethers of the 3:7-dimethyluric acid series (Biltz and Damm, A., 1914, i, 1093) or the 5-alkyloxy-1:7-dimethyl- ψ -uric acid according to the experience of Biltz and Heyn (preceding abstract). It proves to be neither of these, but to be identical with the 4-hydroxy-5-alkyloxy-3:7-dimethyl-4:5-dihydrouic acid obtained by Biltz and Damm (*loc. cit.*). This identity would be easily explicable if the substance could be regarded as being actually 5-alkyloxydimethyl- ψ -uric acids, because it is quite clear that the same product must be obtained from 4:5-dialkyloxy-1:7-dimethyl- and -3:7-dimethyl-4:5-dihydrouic acids. This view, however, is quite untenable for several reasons: (1) the substances are much too stable to be ψ -uric acid; (2) they cannot be reduced to dimethyl- ψ -uric acid by any means, but yield 1-methylhydantoin, so that they must be nearly related to the 3:7-dimethyluric acid glycol, which also yields 1-methylhydantoin; and (3) they yield 3:7-dimethyluric acid glycol by hydrolysis. The formation of 4-hydroxy-5-alkyloxy-3:7-dimethyl-4:5-dihydrouic acid from 4:5-dialkyloxy-1:7-dimethyl-4:5-dihydrouic acid by hydrochloric acid is, therefore, not a simple hydrolysis of the alkyloxy-group in position 4, but is due to the fission of the ether to 5-alkyloxydimethyl- ψ -uric acid, this unstable substance then undergoing isomerisation, the glyoxaline ring being reformed in such a way that 4-hydroxy-5-alkyloxy-3:7-dimethyl-4:5-dihydrouic acid is produced. The correctness of this view has been proved by the synthesis of the 5-alkyloxydimethyl- ψ -uric acid and its actual conversion into the last-mentioned compound. 5-Chloro-1:7-dimethyl- ψ -uric acid,



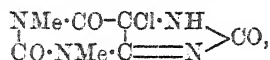
m. p. 222 — 223° (decomp.; reddening at about 80°), obtained by passing chlorine into a mixture of dry chloroform and 1:7-dimethyl- ψ -uric acid, is reduced to 1:7-dimethyl- ψ -uric acid by hydrogen iodide in glacial acetic acid at the ordinary temperature and to 1:7-dimethyluric acid by hydriodic acid on the water-bath, and reacts smoothly with methyl alcohol in the presence of pyridine to form 5-methoxy-1:7-dimethyl- ψ -uric acid, $\text{C}_9\text{H}_{12}\text{O}_5\text{N}_4$, microscopic leaflets, which by rapid heating reddens at about 80 — 90° and has m. p. 173 — 174° (decomp.), but when slowly heated softens at about 170° , becomes hard again at about 180° , and then has m. p. 230 — 240° owing to its conversion into 4-hydroxy-5-methoxy-3:7-dimethyl-4:5-dihydrouic acid. The same change is effected by

crystallising the substance from water. The preceding hemi-ether is obtained directly from 5-chloro-1:7-dimethyl- ψ -uric acid and methyl alcohol in the absence of pyridine, and also by passing chlorine into a mixture of 1:7-dimethyl- ψ -uric acid and methyl alcohol at 0°.

C. S.

Derivatives of 1:3-Dimethyluric Acid. HEINRICH BILTZ and KARL STRUFE (*Annalen*, 1916, **413**, 155—179).—In view of the results obtained in the case of 1:7-dimethyluric acid (Biltz and Damm, preceding abstract), it becomes of interest to examine the behaviour of 1:3-dimethyluric acid and its derivatives under similar conditions. Observations already recorded show that the action of chlorine on uric acids in certain solvents, such as chloroform or glacial acetic acid, produces 5-chloro-*isouric* acids or 5-chloro- ψ -uric acids, the former being usually obtained when the uric acid is alkylated in position 7, for example, 1:3:7-trimethyluric acid (Biltz, A., 1911, i, 168), 3:7-dimethyluric acid (Biltz and Damm, A., 1914, i, 1093), and 1:7-dimethyluric acid (*ibid.*, preceding abstract) whilst uric acid itself, 1-methyluric acid, and 9-methyluric acid yield 5-chloro- ψ -uric acids. It is now found that 1:3-dimethyluric acid behaves in accordance with this rule, but the chloro-*isouric* acid has also been obtained by a peculiar reaction.

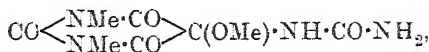
5-Chloro-1:3-dimethyl- $\Delta^{4(9)}$ -isouric acid,



narrow leaflets, m. p. 225° (decomp.), is obtained by passing chlorine into a well-dried solution of anhydrous theophylline in glacial acetic acid at the ordinary temperature, a particle of iodine being added to act as a catalyst. It resembles other chloro-*isouric* acids in its properties. It is very hygroscopic, is reduced to 1:3-dimethyluric acid by hydriodic acid, D 1.96, on the water-bath, or, better, by a saturated solution of hydrogen iodide in glacial acetic acid, is converted into 4:5-dihydroxy-1:3-dimethyl-4:5-dihydrouric acid by water, and reacts with methyl and ethyl alcohols to form 4:5-*dimethoxy*-1:3-dimethyl-4:5-dihydrouric acid, $\text{C}_8\text{H}_{14}\text{O}_5\text{N}_4$, six-sided leaflets, m. p. about 200°, and the corresponding 4:5-*diethoxy*-compound, $\text{C}_{11}\text{H}_{18}\text{O}_5\text{N}_4$, leaflets, m. p. about 163—165°. These ethers, which can also be prepared by the action of chlorine on a mixture of 1:3-dimethyluric acid and the requisite alcohol at 0°, lose 1 mol. of the alcohol by heating at 150—160°/15—20 mm., and are thereby converted into 5-methoxy-1:3-dimethyl- $\Delta^{4(9)}$ -isouric acid, $\text{C}_8\text{H}_{10}\text{O}_4\text{N}_4$, elongated, pointed leaflets, m. p. 207°, and the corresponding 5-ethoxy-compound, irregular prisms, m. p. 195°. These two substances, which are also obtained from 5-chloro-1:3-dimethyl-*isouric* acid and the alcohols in the presence of pyridine, are converted into the 4:5-dialkyloxy-1:3-dimethyl-4:5-dihydrouric acids by methyl and ethyl alcohol containing hydrogen chloride.

The 4:5-dialkyloxy-1:3-dimethyl-4:5-dihydrouric acids are reduced to 1:3-dimethyluric acid by sodium amalgam or by hydriodic acid, D 1.96, on the water-bath, and to 1:3-dimethyl- ψ -uric acid by

hydriodic acid, D 1.5, at about 60°. When warmed with 5% hydrochloric acid or dissolved in concentrated hydrochloric acid at the ordinary temperature they suffer hydrolysis of the alkyloxy-group in position 4 and fission of the glyoxaline ring, yielding thereby 5-methoxy-1:3-dimethyl- ψ -uric acid,



stout rhombohedra, m. p. about 186° (decomp.), and the corresponding 5-ethoxy-compound, $\text{C}_9\text{H}_{14}\text{O}_5\text{N}_4$, felted needles, m. p. 180° (decomp.). These two substances, which can also be obtained (i) by the action of chlorine on a mixture of 1:3-dimethyluric acid and the alcohol without cooling, (2) in a similar way from 1:3-dimethyl- ψ -uric acid, and (3) from 5-chloro-1:3-dimethyl- ψ -uric acid (see below), are proved to be derivatives of ψ -uric acid by the reddening and decomposition accompanying their fusion, by their formation by method (2) above, and by their reduction to 1:3-dimethyl- ψ -uric acid by sodium amalgam or hydriodic acid. 5-Methoxy-1:3-dimethyl- ψ -uric acid has also been obtained by warming 5-chloro-1:3-dimethylsouric acid with methyl alcohol and keeping the solution overnight in a closed flask, the 4:5-dimethoxy-1:3-dimethyl-4:5-dihydrouric acid initially formed (see above) doubtless reacting with the hydrogen chloride generated to form the final product. 5-n-Propoxy-1:3-dimethyl- ψ -uric acid, $\text{C}_{10}\text{H}_{16}\text{O}_5\text{N}_4$, elongated, pointed leaflets, m. p. 177° (decomp.), which slowly separates from a solution obtained by triturating 5-chloro-1:3-dimethylsouric acid with propyl alcohol, doubtless owes its formation to a similar cause.

5-Chloro-1:3-dimethyl- ψ -uric acid, $\text{C}_7\text{H}_6\text{O}_4\text{N}_4\text{Cl}$, small rhombohedra, m. p. 140° (decomp.), is obtained by the action of chlorine on a mixture of 1:3-dimethyluric acid or 1:3-dimethyl- ψ -uric acid and glacial acetic acid. It is unique among the chloro- ψ -uric acids in crystallising without acetic acid of crystallisation. It is converted into 4:5-dihydroxy-1:3-dimethyl-4:5-dihydrouric acid (Biltz and Strufe, A., 1914, i, 586) by water; into the 5-alkyloxy-1:3-dimethyl- ψ -uric acid by warming with methyl or ethyl alcohol containing a little glacial acetic acid, and into 1:3-dimethyl- ψ -uric acid by reduction with hydrogen iodide in glacial acetic acid on the water-bath.

By dissolving 5-methoxy- or 5-ethoxy-1:3-dimethyl- ψ -uric acid in 4*N*-sodium hydroxide and acidifying the solution with concentrated hydrochloric acid, 4-hydroxy-5-methoxy-1:3-dimethyl-4:5-dihydrouric acid, $\text{C}_8\text{H}_{12}\text{O}_5\text{N}_4 \cdot \text{H}_2\text{O}$, prisms, m. p. 241° (decomp.), and the corresponding 4-hydroxy-5-ethoxy-compound, prisms, m. p. 244° (decomp.), are obtained. These substances, the latter of which is also obtained, together with 1:3-dimethyl- ψ -uric acid, by the reduction of 5-ethoxy-1:3-dimethyl- ψ -uric acid by sodium amalgam, are remarkably stable. They can be sublimed without decomposition under reduced pressure, are not attacked by concentrated nitric acid on the water-bath or by a saturated solution of hydrogen iodide in glacial acetic acid at 130°, but are converted by hydriodic acid, (D 1.96), at 130° into a substance, $\text{C}_5\text{H}_7\text{O}_3\text{N}_3$, leaflets, m. p. 257°

(decomp.), which has not been identified; they are oxidised to dimethylparabanic acid by boiling dilute sulphuric acid and potassium dichromate. C. S.

Derivatives of 1:3:7-Trimethyluric Acid. HEINRICH BILTZ and MYRON HEYN (*Annalen*, 1916, 413, 179—185).—4:5-Dimethoxy-1:3:7-trimethyl-4:5-dihydrouric acid, first prepared by Fischer in 1882, is quite readily obtained, in 85% yield, by the vigorous action of chlorine on a mixture of finely powdered caffeine and methyl alcohol below 20°. The diethoxy-compound cannot be prepared in a similar manner. Both substances are reduced to 1:3:7-trimethyluric acid by sodium amalgam or by hydriodic acid under various conditions, attempts to isolate 1:3:7-trimethyl- ψ -uric acid being unsuccessful.

4:5-Dimethoxy-1:3:7-trimethyl-4:5-dihydrouric acid is converted by aqueous hydrogen chloride (saturated at 0°) at 0° into 5-methoxy-1:3:7-trimethyl- ψ -uric acid, $C_9H_{14}O_5N_4$, pyramidal prisms, m. p. 189—191° (decomp.), the filtrate depositing a small quantity of apocaffeine after long keeping; the latter becomes the main product of the reaction when ordinary concentrated hydrochloric acid is used. 5-Methoxy-1:3:7-trimethyl- ψ -uric acid, which has also been prepared by the action of chlorine on a mixture of 1:3:7-trimethyl- ψ -uric acid and methyl alcohol, is converted into apocaffeine by concentrated sulphuric acid, and is reduced to 1:3:7-trimethyl- ψ -uric acid by sodium amalgam.

Attempts to prepare 5-chloro-1:3:7-trimethyl- ψ -uric acid by the action of chlorine on a mixture of 1:3:7-trimethyluric acid and glacial acetic acid containing 1 mol. of water yielded only 5-chloro-1:3:7-trimethylisouric acid (Biltz, A., 1911, i, 168). C. S.

Derivatives of 3:7:9-Trimethyluric Acid. HEINRICH BILTZ and PAUL DAMM (*Annalen*, 1916, 413, 186—197).—3:7-Dimethyluric acid and theobromine are converted into 1:3:7-trimethyluric acid and caffeine respectively by shaking with aqueous sodium hydroxide and methyl sulphate. Under similar conditions, 4:5-dihydroxy-3:7-dimethyl-4:5-dihydrouric acid, 4-hydroxy-5-methoxy- and 5-ethoxy-3:7-dimethyl-4:5-dihydrouric acids, and 4-hydroxy-3:7-dimethyl-4:5-dihydrouric acid (Biltz and Damm, A., 1914, i, 1094) are also methylated, but in these four cases the new methyl group enters into position 9. The proof of this in the case of the first of the four substances is given by the fact that the product, 4:5-dihydroxy-3:7:9-trimethyl-4:5-dihydrouric acid, $C_8H_{12}O_5N_4$, stout rhombohedra, m. p. 200—201° (decomp.), is also obtained by the action of chlorine on a mixture of 3:7:9-trimethyluric acid and water at 80°; this substance has also been obtained in the case of the other three products, which therefore also contain the new methyl group in position 9.

4:5-Dihydroxy-3:7:9-trimethyl-4:5-dihydrouric acid is a strikingly stable substance, and therefore differs in this respect from 4:5-dihydroxy-1:3:7-trimethyl-4:5-dihydrouric acid, which is so

unstable that it has not been isolated, reactions intended to produce it yielding instead its degradation product, *apocaffeine* (Biltz and Krebs, A., 1910, i, 523). The stability of the glycol obtained by methylating 4:5-dihydroxy-3:7-dimethyl-4:5-dihydrouric acid is therefore an indirect proof of its constitution, because the new methyl group cannot be in position 1 (in which case the product must be the unstable 1:3:7-trimethyluric acid glycol), and therefore by exclusion must be in position 9. A second indirect proof of its constitution is furnished by the conversion of 4:5-dihydroxy-3:7:9-trimethyl-4:5-dihydrouric acid into *allocaffeine* by prolonged heating with glacial acetic acid on the water-bath; this is explained by the rupture of the glycol into monomethylalloxan and *s*-dimethylcarbamide, these then reacting to give *allocaffeine* (Biltz, A., 1910, i, 522).

4-Hydroxy-5-ethoxy-3:7:9-trimethyl-4:5-dihydrouric acid, $C_{10}H_{16}O_5N_4$, long prisms, m. p. 175° , is obtained by methylation, as stated above, and also by the action of chlorine on a mixture of 3:7:9-trimethyluric acid and anhydrous ethyl alcohol; it yields 1:3-dimethylparabanic acid by oxidation with sulphuric acid and potassium dichromate, and 4:5-dihydroxy-3:7:9-trimethyl-4:5-dihydrouric acid by hydrolysis with concentrated sulphuric acid and a few drops of water. *4-Hydroxy-5-methoxy-3:7:9-trimethyl-4:5-dihydrouric acid*, $C_9H_{14}O_5N_4$, plates, m. p. 185° , is obtained by the same two methods as the homologous ethoxy-compound, and also yields 4:5-dihydroxy-3:7:9-trimethyl-4:5-dihydrouric acid by hydrolysis.

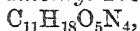
4-Hydroxy-3:7:9-trimethyl-4:5-dihydrouric acid, small rhombohedra, m. p. $196-197^\circ$, prepared by methylation as stated above, is converted into 4-hydroxy-5-ethoxy-3:7:9-trimethyl-4:5-dihydrouric acid and the corresponding 4:5-dihydroxy-compound respectively by the action of chlorine on its mixture with ethyl alcohol and on its solution in water.

Attempts to prepare 5-chloro-3:7:9-trimethyl- ψ -uric acid or 4:5-dichloro-3:7:9-trimethyl-4:5-dihydrouric acid by the action of chlorine on a mixture of 3:7:9-trimethyluric acid and chloroform or glacial acetic acid have been unsuccessful, the only product isolated being *allocaffeine*. C. S.

Derivatives of 1:3:7:9-Tetramethyluric Acid. HEINRICH BILTZ and KARL STRUPE (*Annalen*, 1916, 413, 197-206).—It has been observed that the number of derivatives obtainable from the trimethyluric acids by the author's methods is much smaller than in the cases of the di- and mono-methyluric acids and uric acid itself. This is partly due to the greater solubility of the expected products, but still more so to their greater reactivity, in consequence of which they change into stable degradation products. In the case of tetramethyluric acid, only two derivatives have been obtained, apart from *allocaffeine* and 1:3:7:9-tetramethyl-5:5-*spirohydantoin*, which are already known.

1:3:7:9-Tetramethyluric acid can be conveniently prepared in good yield and in large quantities from caffeine by Wislicenus and

Körber's method (1902). By treating a mixture of the acid and methyl alcohol with chlorine at the ordinary temperature, 4:5-dimethoxy-1:3:7:9-tetramethyl-4:5-dihydrouric acid,



stout prisms, m. p. 133° , is obtained, which is reduced to tetramethyluric acid by hydrogen iodide in glacial acetic acid on the water-bath, and is converted into *allocaffeine* by boiling dilute hydrochloric acid, by hydrochloric acid saturated at 0° , or by alcoholic hydrogen chloride, the hemi-ether, the glycol, or 5-methoxytetramethyl- ψ -uric acid not being produced. 4:5-Diethoxy-1:3:7:9-tetramethyl-4:5-dihydrouric acid cannot be prepared by the action of chlorine on a mixture of tetramethyluric acid and ethyl alcohol; at the ordinary temperature the product is *allocaffeine*, whilst at 0° or in a freezing mixture of ice and sodium chloride, 5-ethoxytetramethyl- ψ -uric acid, $\text{C}_{11}\text{H}_{18}\text{O}_5\text{N}_4$, leaflets, m. p. 215° (decomp.), together with a little *allocaffeine*, is obtained. The ethoxytetramethyl- ψ -uric acid is converted into *allocaffeine* by boiling dilute hydrochloric acid, and is reduced to tetramethyluric acid by hydriodic acid, D 1.96 or 1.5, on the water-bath, and to *allocaffeine* by hydrogen iodide in glacial acetic acid with cooling by water. C. S.

Acyl Derivatives of Paradiazoinbenzene. GILBERT T. MORGAN and ADOLPH WILLIAM HENRY UPTON (T., 1917, 111, 187—196).—In extension of the earlier work on the formation of *p*-diazoinimides from various substitution derivatives of *p*-phenylenediamine (T., 1910, 97, 48; 1908, 93, 614; 1907, 91, 1505, etc.), it has now been discovered that formyl-*p*-phenylenediamine and its homologues can be converted into *p*-diazoinimides by diazotising with liquid nitrogen trioxide in acetone. In this manner, there have been obtained formyl-*p*-phenylenediazoinimide, $\text{N}_2\text{—C}_6\text{H}_4\text{—N—COH}$, acetyl-*p*-phenylenediazoinimide, benzoyl-*p*-phenylenediazoinimide, and benzoyl-1:4-naphthylenediazoinimide, $\text{C}_{10}\text{H}_6\text{—N}_2\text{—N—C(=O)Bz}$. The substances of higher molecular weight are more stable than their lower analogues; all are able to couple with β -naphthol, with formation of an azo-compound.

For experimental details see the original.

D. F. T.

The Bisulphite Compounds of Azo-colouring Matters. N. N. VOROSHOV (*Ann. Chim.*, 1916, [ix], 6, 381—403; 1917, [ix], 7, 50—113).—A full account of work already published (compare A., 1916, i, 293). W. G.

The Chemistry of the Proteins. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1917, 78, 349—353).—When serum is dried in a film on a glass plate, a product is obtained which is soluble in water. If, however, the product is ground up in a mortar, a powder is formed which is no longer completely soluble.

The following explanation is offered of this "mechanical denaturation" of the protein. The scale preparation is considered to consist of spheres of the protein surrounded by a layer of protein degradation products, to the presence of which the disaggregation of the protein in water is due. By grinding in a mortar, the spheres are broken up, and fresh surfaces are exposed on which there are no degradation products, and owing to the exposure of surfaces of protein without these products, complete solubility is no longer possible.

S. B. S.

Behaviour of Casein toward Dilute Solutions of Sodium Chloride. SIGFRID RYD (*Zeitsch. Elektrochem.*, 1913, 23, 19—23).—After a short discussion on the behaviour of casein toward acids bases and salts generally, and a discussion of the amphoteric character of this substance, the author describes a number of experiments made to determine the solubility of casein in dilute solutions of sodium chloride at 18—20°. A weighed quantity of casein was placed in a measured quantity of sodium hydroxide solution and stirred rapidly until all had dissolved. Then from a burette sufficient hydrochloric acid was added to neutralise the whole of the sodium hydroxide. This precipitated the major portion of the casein, and formed sodium chloride. Then, by the cautious addition of dilute sodium hydroxide and hydrochloric acid, a point was reached at which the addition of a further drop of hydrochloric acid would just produce an opalescence. When this was the case, the solution was saturated with casein. It is shown that the solubility reaches a maximum in sodium chloride solution of 0.1114*N*, and then decreases.

J. F. S.

Achroodextrinase. J. EFFRONT (*Compt. rend.*, 1917, 164, 415—416).—Certain species of *Bacillus mesentericus*, grown in a nitrogenous medium, secrete a diastase which liquefies starch. The author has isolated this diastase, which he calls *achroodextrinase*, and examined its properties. It rapidly converts amylo- and erythro-dextrin into achroodextrin, but it only possesses a very limited saccharifying power. It hydrolyses starch, giving about 40% of maltose, at which point the amylo- and erythro-dextrins are destroyed and the saccharification is completely stopped. Achroodextrinase is also distinguished from other amylases in that the products of saccharification have a much lower viscosity. This new diastase is precipitated by alcohol and by ammonium sulphate. Its optimum temperature is 40°. It acts very well in neutral solutions, and is very resistant to alkalis, but very sensitive to acids.

W. G.

Ivy-peroxydase, a Gluco-protein, and G. Woker's Aldehyde-Hypothesis of the Peroxydases. A. W. VAN DER HAAR (*Ber.*, 1917, 50, 303—305).—In her recent paper (this vol., i, 61) Woker referred to the author's communication on *ivy-peroxydase* (A., 1910, i, 604) in support of her theory. A protest is raised that

such an interpretation of the conclusions reached by van der Haar was not justified.

J. C. W.

Thiophen Series. VII. Thiophen Compounds containing Mercury or Arsenic. WILHELM STEINKOPF (*Annalen*, 1917, 413, 310—333. Compare A., 1915, i, 155).—It has been shown previously (A., 1914, i, 427) that negatively substituted thiophens behave differently towards mercuric chloride in that 2-halogenothiophens, like thiophen itself, yield normal mercurichlorides, whilst 2-nitrothiophen reacts in another sense. It is now shown that thiophen-2-carboxylic acid in alcoholic solution reacts with cold, saturated mercuric chloride solution and 33% sodium acetate solution to form two amorphous substances, $C_4H_3O_2ClSHg$, decomp. $297-298^\circ$, which behave alike in most respects. They are both soluble in dilute aqueous sodium hydroxide or carbonate, but only one dissolves in dilute ammonia; the other, after solution in alkali hydroxide and reprecipitation by dilute hydrochloric acid, acquires the property of dissolving in dilute aqueous ammonia. The two substances are regarded as two forms of *thiophen-2-mercurichloride-5-carboxylic acid*, $CO_2H \cdot C_4H_3S \cdot HgCl$.

The reaction between sodium iodide (1 mol.) and thiophenmercurichloride previously described (*loc. cit.*) leads to the expectation that by the use of 2 mols. of sodium iodide the formation of the thiophenmercuri-iodide will be superseded and mercury dithienyl produced in almost quantitative yield. This is found to be the case; $2C_4H_3S \cdot HgCl + 4NaI = Hg(C_4H_3S)_2 + 2NaCl + HgI_2, 2NaI$ and $2C_4H_3S \cdot HgI + 2NaI = Hg(C_4H_3S)_2 + HgI_2, 2NaI$. A whole series of thiophen derivatives containing mercury have been examined for their behaviour towards sodium iodide (1 and 2 mols.) in acetone solution. When 1 mol. is used, only 2-iodothiophen-5-mercurichloride behaves like thiophenmercurichloride, and yields a mixture of 2-iodothiophen-5-mercuri-iodide, $C_4H_3IS \cdot HgI$, faintly yellow, microcrystalline substance, m. p. $141-142^\circ$ (to a turbid liquid clarifying at about 165°), and mercury 5:5'-di-iodo-2:2'-dithienyl, $Hg(C_4H_3IS)_2$, pale yellow needles, m. p. 231° ; the other substances examined, 2-chloro- and 2-bromo-thiophen-5-mercurichloride, 3:4-dimethylthiophen-2-mercurichloride and 2:5-dimethylthiophen-3-mercurichloride, are converted only into the corresponding mercuri-iodides when 1 mol. of sodium iodide is used. It has been found that, when mercurichlorides react with 2 mols. of sodium iodide or mercuri-iodides with 1 mol., all derivatives containing mercury in the α -position yield mercury dithienyls, whereas 2:5-dimethylthiophen-3-mercurichloride, the only substance examined containing mercury in the β -position, remains unchanged. If this difference proves to be a general one, the behaviour with sodium iodide in acetone solution is a simple method of distinguishing between the α - and β -derivatives.

All mercury dithienyls behave alike with mercuric haloids in acetone solution, in accordance with the equation $Hg(C_4H_3S)_2 + HgX_2 = 2C_4H_3S \cdot HgX$, where $X = Cl, Br, \text{ or } I$. Mercury diphenyl and di- α -naphthyl also react with mercuric chloride in the sense of this equation.

The following new compounds have been prepared by the preceding methods: 2-chlorothiophen-5-mercuri-iodide, colourless leaflets, m. p. 126—126·5°; mercury 5:5'-dichloro-2:2'-dithienyl, silvery crystals, m. p. 155°; 2-chlorothiophen-5-mercuribromide, felted crystals, m. p. 189—190°; 2-bromothiophen-5-mercuri-iodide, small crystals, m. p. 119°; mercury 5:5'-dibromo-2:2'-dithienyl, felted crystals, m. p. 183°; 2-bromothiophen-5-mercuribromide, felted needles, m. p. 197—197·5°; 2-iodothiophen-5-mercuribromide, almost colourless, felted crystals, decomp. 176° (slowly heated) or about 190° (rapidly heated); 3:4-dimethylthiophen-2-mercuri-iodide, faintly yellow leaflets, m. p. 142°; mercury 3:4:3':4'-tetramethyl-2:2'-dithienyl, felted mass, m. p. 155—156°; 2:5-dimethylthiophen-3-mercuri-iodide, colourless needles, m. p. 175°; and mercury 2:5:2':5'-tetramethyl-3:3'-dithienyl, crystals, m. p. 144—145°, prepared by the old method (*loc. cit.*) of boiling 2:5-dimethylthiophen-3-mercurichloride with sodium in xylene.

[With MARTIN BAUERMEISTER.]—Direct arseniation of the amino- and hydroxy-derivatives of thiophen is impracticable owing to the difficulty of preparing these substances. Arsenic trichloride, however, reacts with mercury dithienyls or thiophenmercurihaloids in some cases (compare Finzi, A., 1916, i, 94; Finzi and Furlotti, *ibid.*, i, 95). Thus, when arsenic trichloride is shaken in the cold with powdered mercury 2:2'-dithienyl and the product is distilled in a vacuum in an atmosphere of hydrogen, fractions are obtained from which the following have been isolated: (1) *thienyldichloroarsine*, $C_4H_3S \cdot AsCl_2$, faintly brown liquid with an unpleasant odour, b. p. 118—122°/11 mm.; (2) *dithienylchloroarsine*, $(C_4H_3S)_2AsCl$, b. p. 219—232°/13 mm.; and (3) *trithienylarsine*, $(C_4H_3S)_3As$, faintly yellowish-green, almost odourless, viscous liquid, b. p. 199—200·5°/0·5 mm. Dithienylchloroarsine, b. p. 106—110°/0·5 mm., is the chief product isolated when thiophen-2-mercurichloride and arsenic trichloride are heated in boiling toluene for many hours, and the product is distilled in the vacuum of a Gaede pump. C. S.

Physiological Chemistry.

Oxyhæmoglobin Crystals from the Blood of Guinea-pigs. OTTO KRUMMACHER (*Zeitsch. Biol.*, 1917, 67, 272—278).—The crystals of oxyhæmoglobin of the blood of guinea-pigs are not regular tetrahedra, but sphenoids belonging to the rhombic system. S. B. S.

Cataphoretic Investigations with Thrombin and Fibrinogen. ALFRED RESCH (*Biochem. Zeitsch.*, 1917, 78, 297—307).—Thrombin, or its negatively charged part, wanders towards the

anode. It dissociates partly into $(R\langle\text{NH}_3^+\text{X}\rangle^-)$ and Ca^+ and partly with the formation of complex organic cations and anions; the anodic complex probably holds calcium in a physically adsorbed form. The charge on the thrombin or its anion is not influenced by the acidity of the solution varying between $p_{\text{H}}=5$ and $p_{\text{H}}=8$. Fibrinogen acts as an electrically neutral substance. The author discusses the bearing of his results on the mechanism of clotting.

S. B. S.

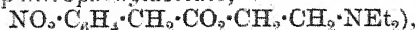
The Influence of Extracts of the Genital Glands on Phosphorus Metabolism. JEAN (*Compt. rend.*, 1917, 164, 438—440).—The injection of an extract of the interstitial gland from the testes of pigs or of an extract of active yellow bodies from the ovaries of sows causes a marked diminution in the phosphorus excretion of humans, whether on a diet slightly lacking in phosphorus or containing it in slight excess.

W. G.

The Sulphur Compounds of the Urine. E. SALKOWSKI (*Biochem. Zeitsch.*, 1917, 79, 68—80).—Thiosulphate is found in the urine of rabbits after feeding on cabbage. The precursor of this is to be found in the aqueous extract of the vegetables, but not in the residue after extraction of the vegetables with water. No thiosulphate is found in human urine after ingestion of cabbage. Ethyl mercaptan is also found in rabbits' urine after ingestion of cabbage, in the form of an unknown compound, from which it can be obtained after scission with hydrochloric (but not acetic) acid. Ethyl sulphide is found in the urine of dogs in the form of a compound, from which it can be obtained by the action of calcium hydroxide. The parent substance is apparently a sulphonium base. The author reviews the literature dealing with the presence of cystine in urine. Experiments are quoted which seem to indicate that the thiocyanates of urine are derived from glycine. The factors influencing the relationship of "neutral" to the total sulphur of the urine are also discussed.

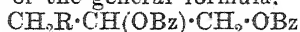
S. B. S.

Relation between Chemical Constitution and Physiological Action in Certain Substituted Aminoalkyl Esters. II. FRANK LEE PYMAN (*T.*, 1917, 111, 167—172. Compare *T.*, 1908, 93, 1793).—It is already known that the substitution of benzoyl by phenylacetyl in cocaine yields a product devoid of local anæsthetic properties, whereas with α -eucaine a similar change produces a compound possessing such properties, and the author has now examined the effect of a similar replacement in anæsthesine (ethyl *p*-aminobenzoate) and novocaine (β -diethylaminoethyl *p*-aminobenzoate). Ethyl *p*-aminophenylacetate (Salkowski, A., 1895, i, 602) dissolved in olive oil and β -diethylaminoethyl *p*-aminophenylacetate, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_2$ (obtained by reduction of the corresponding *p*-nitrophenylacetate,



in the form of an aqueous solution of the hydriodide, were devoid of local anæsthetic power.

In extension of the earlier observation (*loc. cit.*) that the salts of aminoalkyl esters of the general formula,



(where $\text{R} = \text{NMe}_2$, NEt_2 , or $\text{C}_5\text{H}_{10}\text{N}$), possessed considerable local anæsthetic action, but were also toxic and irritant, compounds of a modified type were prepared. By the interaction of phenyl glycid ether and diethylamine there was obtained β -diethylamino- β' -phenoxycispropyl alcohol, $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NEt}_2$, of which the benzoyl derivative gave solutions which were too strongly acidic for satisfactory physiological examination; the hydrochloride of the amino-alcohol, however, in aqueous solution, produced a distinct degree of local anæsthesia. 8-Benzoyloxy-1-methyl-1:2:3:4-tetrahydroquinoline, prepared by benzoylating its parent compound, gave a hydrochloride so strongly acidic that it could not be tested physiologically, and an endeavour to prepare the corresponding p -aminobenzoyl derivative by way of 8- p -nitrobenzoyloxy-1-methyl-1:2:3:4-tetrahydroquinoline miscarried on account of the ease with which the nitrobenzoyl radicle undergoes hydrolytic scission. p -Aminobenzoyl- p -phenetidine, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, prepared by reduction of the corresponding nitro-compound, was found to be almost insoluble in water and caused no local anæsthesia when introduced as a powder into the conjunctival sac. D. F. T.

Anæsthesine and Isethionyl- p -aminobenzoic Acid. E. SALKOWSKI (*Biochem. Zeitsch.*, 1917, 79, 81—95).—An account of experiments, which did not lead to the desired result, for obtaining a soluble compound of anæsthesine (ethyl p -aminobenzoate) is given. Special attention was given to the condensation product of anæsthesine with isethionic acid (compare A., 1916, i, 815). This isethionyl- p -aminobenzoic acid, when administered to rabbits, undergoes scission, and sulphuric acid and (in smaller quantity) thiosulphuric acid are excreted in the urine. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

The Formation of Ferments. MARTIN JACOBY (*Biochem. Zeitsch.*, 1917, 79, 35—50).—The following substances were found to stimulate the formation of a urease by bacteria: dextrose, d -galactose, glycerol, dl -glyceraldehyde, dihydroxyacetone, pyruvic acid, and lactic acid. The stimulatory action of these substances was great. A stimulatory action was shown, but less markedly, by d -lævulose, d - and l -arabinose. Mannose, d -sorbose, rhamnose, heptose, the polysaccharides, glucosides, and the sugar alcohols were without action. S. B. S.

The Production of Phenol by Bacteria. ALBERT BERTHELOT (*Compt. rend.*, 1917, 164, 196—199).—The author has isolated from

the intestinal flora of human subjects suffering from chronic intestinal trouble a bacillus, which he calls *Bacillus phenologenes*, which is capable of producing, under average culture conditions, about ten times as much phenol as the most active known phenologenic species. With *l*-tyrosine as the only organic nutrient, under the most satisfactory conditions it can produce, in fifteen days at 37°, 800 mg. of phenol per litre, the yield thus reaching about 80% of the theoretical yield. The bacillus is anaerobic. W. G.

Biochemical Properties of Paratyphus Bacilli. H. C. DE GRAFF (*Bull. Sci. Pharmacol.*, 1916, **23**, 257—266; from *Chem. Zentr.*, 1917, i, 332).—The decomposition of proteins, peptides, and amino-acids by paratyphus bacilli has been studied, the materials used being centrifuged milk, peptone (Roche and Witte), tryptophan, tyrosine, and alanine. The paratyphus bacillus B degrades proteins and peptides to amino-acids, and can eliminate the amino-group from the latter and oxidise them to acids poorer by one C-atom than the amino-acids themselves. The paratyphus bacillus A acts similarly towards amino-acids, but does not decompose proteins or peptides. The formation of indole from tryptophan or phenol from tyrosine was not observed, but these amino-acids yield indoleacetic acid and *p*-hydroxyphenylacetic acid in addition to small amounts of indolecarboxylic acid and *p*-hydroxybenzoic acid. Alanine gives acetic acid, but not formic acid; Witte's peptone yields tryptophan and indoleacetic acid, and Roche's peptone gives *l*-tyrosine. Both types of bacillus cause the formation of small amounts of acid from the lactose of milk, but only the B variety decomposes the proteins energetically with the liberation of ammonia. Milk treated with litmus is more or less strongly reddened at first by both types of bacillus, but is only quickly coloured blue by the paratyphus bacillus B. H. W.

The Relationship between the Capacity for Killing and Inhibiting the Growth of Germs and the Valency. E. FRIEDBERGER and G. JOACHIMAGLU (*Biochem. Zeitsch.*, 1917, **79**, 135—151).—In experiments with bacteria and protozoa it can be shown that the tervalent arsenic compounds (sodium arsenite and salvarsan) have a greater toxic effect than the quinquevalent compounds (sodium arsenate and atoxyl). A similar difference is noted between the tervalent (tartar emetic) and quinquevalent (potassium pyroantimoniate) antimony compounds. Arsenites inhibit the action of yeast to a greater extent than do arsenates. S. B. S.

Ferment Action. I. The Fermentative Degradation of Polypeptides. EMIL ABDERHALDEN and ANDOR FODOR (*Fermentforschung*, 1916, **1**, 533—596; from *Chem. Zentr.*, 1917, i, 311—313).—The authors have investigated the action of ferments on synthetic polypeptides which are formed from such amino-acids as occur naturally. Even in these circumstances many unknown factors are found to enter into the problem. The physical properties of the substrate in the solution, as well as its chemical constitu-

tion, are of importance, as well as the unexplained condition of the ferment. With respect to the latter, the authors have secured uniformity by performing all comparative experiments with one and the same solution of the ferment prepared in a definite manner. Uniform conditions were also maintained in other respects, and it is emphasised that the results obtained are only valid under these conditions and do not apply, for example, to processes within the cell. Solutions of the ferment were prepared from dried yeast according to Lebedev; it was found that different consignments of the preparation from the same firm showed considerable differences in activity. Strictly comparable experiments were therefore always carried out with the expressed juice of yeast from a single consignment. The juice was fairly acid to litmus, and was therefore nearly neutralised, since otherwise the desired regulation of the solutions could not be obtained. The turbidity caused by neutralisation (obviously protein) disappeared after some hours, particularly rapidly at 25°. Freshly prepared extracts increased in activity when preserved, the maximum being attained more rapidly at 25° than at 0°. Thereby, the optimum of the reaction in experiments with glycyl-L-leucine is displaced in the direction of greater hydroxyl-ion concentration. Addition of very minute amounts of protein to the freshly prepared extracts causes an immediate exaltation of activity which does not then further increase, whilst larger quantities bring about a diminution. Apparently, therefore, surface phenomena are intimately concerned with the increase in activity. To avoid these complications, the yeast-juice was preserved until constant in its behaviour towards glycyl-L-leucine as substrate. The reverse change, namely, decrease in activity due to destruction of the ferment, occurs in older extracts. The greatest stability of peptase occurs with a hydrogen-ion concentration of about 3×10^{-7} ; variation in either direction causes a distinct decomposition after one hour at 25° and the sensitiveness is greater towards an increase in the hydrogen-ion than towards an increase in the hydroxyl-ion concentration. In the experiments described by the authors, in which the duration did not exceed forty minutes and the hydrogen-ion concentration lay generally within the limits $p_H = 6.5-8.5$, the correction involved for this reason was too small to be taken into account.

The rate of fission of glycyl-L-leucine was studied by adding 10 c.c. of a solution containing 0.4 gram of the dipeptide to 20 c.c. of a phosphate solution of the desired hydrogen-ion concentration; the mixture was warmed to 25° and treated with yeast extract (2 c.c.) previously warmed to 25°. The amino-nitrogen was estimated after definite intervals by Sørensen's method in the presence of formaldehyde. Parallel with these experiments, the electromotive force against a 1/10*N*-calomel electrode was measured. Control experiments with mixtures of yeast and regulator, or regulator and polypeptide solution are unnecessary, since they remain unchanged under the experimental conditions. The course of the degradation of the dipeptide at different H^+ and OH^- concentrations was thus followed, and it was found that not merely the rate of reaction but

also its nature is dependent on them. Similar experiments were performed with *d*-alanyl-*d*-leucine; the influence of variation in the amount of ferment on the fission of glycyl-*l*-leucine between p_H 7.5 and p_H 7.13 was also investigated. Similar experiments, but in more dilute solution, were also performed with six dipeptides which form three pairs of isomerides (namely, glycyl-*l*-leucine, *l*-leucylglycine, glycyl-*d*-alanine, *d*-alanylglycine, *d*-alanyl-*l*-leucine, *l*-leucyl-*d*-alanine), in which hydrolysis occurred much more rapidly. The experimental results are expressed in tables and curves.

Increase in the concentration of the yeast extract greatly diminishes the rate of reaction, but this depends also on the reaction and on the amount of yeast peptase present. It is true for glycyl-*l*-leucine in very dilute acid or faintly alkaline solution (p_H = 6.20—7.50) in the presence of an excess of yeast extract, whilst increase of an originally very small amount in this interval increases the amount hydrolysed. Beyond p_H = 8, a quantity of yeast extract which previously diminished the reaction velocity, is found to cause a further increase. In all cases in which the graphs have a parabolic form, the quantity of material hydrolysed is approximately proportional to the square root of the time, and approximately equal amounts of polypeptide are hydrolysed for equal values of $F \times t$ (F = concentration of ferment, t = time). Special experiments have shown that the amino-acids which are formed as products of hydrolysis can exert a powerful retarding action; glycine behaves thus in alkaline, *l*-alanine, and *d*-leucine only in acid solution. This is contrary to the assumption of Herzfeld (A., 1915, i, 468) that the degradation products behave as accelerators.

A specific action of the substrate is certainly concerned with the influence of the concentration of the ferment, but it has not yet been proved whether such action depends on physical characteristics or chemical affinities. Only glycyl-*d*-alanine behaves similarly to glycyl-*l*-leucine, whilst, for example, with *l*-leucylglycine quantities of juice which caused the effects described above bring about a uniform increase in the rate of reaction independent of the acidity of the solution. The course of the reaction is probably mainly governed by diffusion processes. The authors discuss the possibility of explaining the linear course of the reaction in faintly acid solution by assuming the formation of a compound of ferment and substrate or by autocatalytic action, but do not put forward a hypothesis which satisfactorily covers all cases.

The optimal hydrogen-ion concentration has been determined for a number of polypeptides with the following results, the values of p_H being enclosed within brackets: glycyl-*l*-leucine (8.41, 8.50); *l*-leucylglycine (7.50, 7.56); *d*-alanylglycine (7.30—8.13); glycyl-*d*-alanine (7.30—7.91); *d*-alanyl-*l*-leucine (6.76, 6.85); *l*-leucyl-*d*-alanine (6.80—7.89); *dl*-leucyl-*l*-aspartic acid, 2% (6.76); *dl*-leucyl-*l*-aspartic acid, 10% (6.80); *l*-leucylglycylglycine (7.26); *l*-leucyldiglycylglycine (7.29); *l*-leucyltriglycylglycine (7.28); *l*-leucylpentaglycylglycine (6.24).

The optima for the different polypeptides with equal amounts of

ferment depends on their nature, those which are formed from like components showing a generally, but not perfectly uniformly, comparable behaviour. The occurrence of an optimum is regarded as the result of two opposed forces, the diffusion of the substrate into the ferment phase and the adsorption of the fission products by the latter. Both are favoured by hydroxyl ions.

The results which have been obtained support the view that ferments act as colloidal catalysts and are closely connected with the work of Bredig and his co-workers on 'inorganic ferments.' Further experiments are required to determine what causes bring about diffusion to the surface of the disperse ferment phase and whether these are connected with the specific nature of ferment action. The assumption that a ferment is active towards a definite grouping of atoms is not supported by the authors' experiments.

H. W.

The Oxidative Actions of Yeast. G. FÄRBER (*Biochem. Zeitsch.*, 1917, 78, 294—296).—The author finds that, contrary to the experience of Herzog, saligenin is not oxidised to salicylic acid by yeast, nor could he trace any chemical changes of thymol and cymol.

S. B. S.

The Detection of Tyrosol and Tryptophol in Products of Fermentation. FELIX EHRLICH (*Biochem. Zeitsch.*, 1917, 79, 232—240).—In the case of wine, the liquid is evaporated to a syrup in a vacuum, the residue dissolved in alcohol, the solvent distilled off, and the residue thus obtained heated with a 10% solution of sodium hydroxide, to saponify the esters of the alcohols. The tryptophol is extracted from this alkaline liquid by ether. If no crystals of tyrosol can be obtained, its presence can be determined by the author's dimethylaminobenzaldehyde reagent, which gives a characteristic bluish-red colour on warming and addition of hydrochloric acid, the product being soluble in amyl alcohol, in which solution it can be examined spectroscopically. The tyrosol can be obtained from the alkaline solution (after the saponification with sodium hydroxide as mentioned above) by making this first slightly acid with sulphuric acid, then slightly alkaline with sodium hydrogen carbonate, and then extracting for twenty hours with ether. After distilling off the ether, a residue is obtained which yields crystals of tyrosol; this can also be obtained in the form of its dibenzoyl derivative. Similar methods for obtaining tyrosol and tryptophol can be applied to beer and mash.

S. B. S.

The Vegetation of Yeasts and Moulds on Heterocyclic Nitrogen Compounds and Alkaloids. FELIX EHRLICH (*Biochem. Zeitsch.*, 1917, 79, 152—161).—Experiments were carried out with the following organisms: *Willia anomala*, *Oidium lactis*, *Pichia farinosa*, *Penicillium glaucum*, *Aspergillus niger*, and the following nitrogenous substances: pyridine, piperidine tartrate, coniine, nicotine, cinchonic acid, quinine, brucine, cocaine, and morphine. It was shown that these could serve as a source of nitrogen to the organisms.

S. B. S.

Production of Pyruvic Acid by Biochemical Oxidation of Lactic Acid. P. Mazé and M. Rtor (*Compt. Rend. Soc. Biol.*, 1916, 79, 706—710. Compare Mazé, A., 1913, i, 567; Fernbach and Schoen, A., 1914, i, 237, 910).—*Amylomyces Rouzii* (a mould related to *Mucor*) and another undetermined fungus, parasitic on maize, oxidise lactic acid to pyruvic acid in a solution containing no other carbon compound, and ultimately also destroy the pyruvic acid formed. The yield is better with free lactic acid than with calcium lactate, for in the latter case the solution becomes alkaline and growth is inhibited. As may be foreseen, the respiratory quotient is low (0.77—0.90). Similar effects may be obtained with sucrose in thin layers of a solution not more concentrated than 1 per cent. (in order to avoid the formation of alcohol). G. B.

Evidence of the Existence in Malt of an Enzyme Hydrolysing the Furfuroids of Barley. JULIAN LEVETT BAKER and HENRY FRANCIS EVERARD HULTON (*T.*, 1917, 111, 121—130).—Having observed the presence of a slightly increased percentage of furfuroids (furfuraldehyde-yielding matter) in rootlet-free malt as compared with the original barley, and that in the rootlets and husks of the malt the furfuroid content is higher than in the barley as a whole, the authors allowed embryos excised from barley to germinate in the dark on sterilised sand soaked with sucrose solution, and found an increase in weight and in furfuroid content, the embryo presumably having effected the conversion of sucrose into a poly-pentose.

When allowed to germinate between damp linen in a normal manner, barley corns were found to undergo no increase in total furfuroid content, the increased furfuroid content of the embryo being approximately equal to the corresponding diminution observed in the endosperm. This result appears to indicate the existence of an enzyme capable of hydrolysing insoluble furfuroids in the non-embryo portion of the grain, so that the soluble products may be transferred to the embryo. Confirmation of this view is supplied by the facts that malt contains a higher proportion of soluble furfuroids than the corresponding barley, and that a mixture of green malt and barley when digested with water at 35° gives a higher yield of soluble furfuroid matter than the average for barley and malt separately; also it was found that the enzymes, which are precipitated on the addition of an aqueous infusion of malt to alcohol, when dissolved in water are capable of hydrolysing 10% of the insoluble furfuroids of purified malt husks to soluble furfuraldehyde-yielding substances. The evidence therefore indicates the existence in green malt of a "pentosase" capable of hydrolysing insoluble furfuroids. D. F. T.

The Organic Matter of the Soil. I. Some Data on Humus, Humus Carbon, and Humus Nitrogen. ROSS AIKEN GORTNER (*Soil Sci.*, 1916, 2, 395—441).—"Humus" extracts were made from seventeen samples representing soils, peats, and fresh

vegetable matter, 4% ammonia solution being used with and without a preliminary leaching with 1% hydrochloric acid. The humus obtained was very similar in all cases, indicating that it is not a typical soil product, but may also be obtained from unchanged vegetable matter. When the ammonia was replaced by a 4% solution of sodium hydroxide in the preparation of the extracts, neither the same substances nor the same quantity of the substances were obtained, the extracts with sodium hydroxide containing more carbon and being less deeply coloured.

The nitrogen compounds in the soil were shown to be somewhat more insoluble than those in fresh vegetable matter by the fact that 1% hydrochloric acid dissolved 20% of the total nitrogen from the fresh vegetable matter and only 3—4% from the soils and peats; also that whilst about 30% of the nitrogen in the soils was insoluble in the sodium hydroxide, the nitrogen in the fresh vegetable matter was dissolved almost completely.

When the samples were treated successively with 4% sodium hydroxide, with 1% hydrochloric acid, again with sodium hydroxide, and finally shaken up with water, the fresh vegetable matter and an acid peat yielded colourless solutions, but in the case of all the other soils jet-black solutions were obtained, from which "soil pigment" was precipitated by acids or alkalis. Having estimated the amount of carbon in this black pigment, it was calculated that probably not more than 30—40% of the humus (so-called "matière noire" of Grandeau) dissolved by ammonia could be made up of really black compounds, the rest consisting of colourless substances. The author points out that the black pigment appears to be the only substance which can be said to be a true soil product. It contains only a relatively small proportion of the soil nitrogen, and would seem to have but little importance in the problem of soil fertility.

L. M. U.

The Organic Matter of the Soil. III. The Production of Humus from Manures. ROSS AIKEN GORTNER (*Soil Sci.*, 1917, 3, 1—8).—Organic matter, in the shape of powdered silk waste, powdered wool, flour, or lucerne meal was added to soil at the rate of 3—7% of the soil. Each mixture was put into a pot in a greenhouse and left for a year, so that humification should take place. Estimations of carbon, nitrogen, and "humus" soluble in 4% ammonia were made on the original mixtures and on the final product. They were considerably lower after storage than before, the losses amounting to from 8 to 55% of the original carbon, from 5 to 26% of the original nitrogen, and from 6 to 33% of the original "humus." The author is of opinion that the maximum amount of "humus" is therefore present in a soil immediately after a green manure crop has been ploughed in and before the "humifying" bacteria or fungi have begun their work.

L. M. U.

Soil Solution obtained by the Action of a Hydraulic Press. G. RAMANN, S. MÄRZ, and H. BAUER (*Int. Mit. Bodenkunde*, 1916, 6, 27; from *Bied. Zentr.*, 1917, 46, 6).—The authors point

out that the analysis of drainage waters from soils does not afford an accurate means of determining the composition of the normal soil solution, as drainage only occurs when the soils are super-saturated. For this reason they adopted the method of forcing water out of the soil with a hydraulic press. Samples of 3 kilos. of soil were taken from the fields and subjected to a pressure of 300 kilos. to the square cm., the liquid expressed being then analysed for calcium, magnesium, sulphates, phosphoric acid, and potassium. The sampling was done on six different occasions over a period lasting from May to October; both surface and subsoil were used.

The calcium content was found to vary considerably in the surface soil, but in the subsoil it seemed fairly constant, except for a rise in mid-summer. Potassium, contrary to the generally accepted view, behaved very much like calcium, that is, its content fluctuated according to the general concentration of the soil solution, rising when evaporation took place and being lowered by spells of wet weather. Further, there was evidence of potassium and calcium being transported from the subsoil to the surface during a prolonged period of drought, but no evidence was obtained that adsorption exerted any regulating effect on the concentration of the soil solution. The exchange of bases only occurred when the proportion which the dissolved substances bore to one another was altered.

The authors suggest that the selective action of the plant roots, by throwing the soil solution out of equilibrium, would have a considerable effect in bringing fresh supplies of nutrient substances into solution. They state also that the pressure method of obtaining soil water is only applicable in the case of soils made up of very fine particles or containing a considerable amount of humus.

L. M. U.

Criticism of the Use of Superphosphates in Agriculture.

NICOLA ALBERTO BARBIERI (*Gazzetta*, 1917, 47, i, 38—51).—From the results of a number of experiments the author draws the following conclusions: The whole of the phosphorus contained in plants occurs in the form of phosphoric acid united with alkalis, alkaline earths, and possibly other mineral bases. When the soluble and the insoluble phosphates are eliminated, the plant contains no trace of any other compound of phosphorus; phytins are, consequently, lacking. Plants do not contain and do not absorb mono- or di-calcium phosphates (superphosphates). Superphosphate exerts a retarding action on the germination of seeds and on the development of plants, and cereals and leguminous plants grown in soil fertilised by means of superphosphate contain less total phosphorus than those from contiguous soil not treated with the superphosphate. Further, superphosphate destroys seeds with which it comes into direct contact. Where mineral fertilisation is to be effected it is best to apply those mineral substances which the plants themselves contain.

T. H. P.

Organic Chemistry.

Action of Bromine Water on Ethylene. JOHN READ and MARGARET MARY WILLIAMS (T., 1917, 111, 240—244).—It has already been observed (Pope and Read, T., 1912, 101, 760) that bromine water in its action on indene behaves like a solution of hypobromous acid, yielding bromohydroxyhydrindene, and it is now shown that bromine water exhibits a similar reaction with ethylene, giving ethylene bromohydrin accompanied by an approximately equal weight of ethylene dibromide. This behaviour is evidently due to the existence of the equilibrium $\text{Br}_2 + \text{H}_2\text{O} = \text{HBr} + \text{HOBr}$.

For experimental details see the original.

D. F. T.

Pyrogenic Acetylene Condensations. IV. RICHARD MEYER and HANS WESCHE (Ber., 1917, 50, 422—441. Compare A., 1912, i, 525; 1913, i, 1294; 1915, i, 207).—Mixtures of acetylene with hydrogen sulphide, ammonia, or steam have been heated in the electric oven already described in order to find whether the resultant tars contained any of the phenolic or heterocyclic compounds found in coal tar. The treatment of the tar is fully described, and the original should be consulted for the details.

Acetylene and hydrogen sulphide are found to react at 640—660° to form thiophen, and most probably thionaphthen and thiophthen. Acetylene, purified coal gas (equivalent to methane), and hydrogen sulphide give α - or β -thiotolene (identified as *tetrabromothiotolene*, $\text{C}_4\text{Br}_3\text{S}\cdot\text{CH}_2\text{Br}$, pale yellow, pearly leaflets, m. p. 113—114°), thioxens (colour reactions), thionaphthen, and thiophthen (from which *tetrabromothionaphthen*, very long, slender needles, m. p. 229—230°, was prepared and analysed).

Acetylene and ammonia give pyridine, pyrrole, aniline, benzonitrile, naphthalene, quinoline, indole (?), fluorene, and anthracene.

With steam, the condensation proceeds at a lower temperature (500—600°), and a small quantity of phenol is obtained. Acetylene, steam, and ammonia together give pyridine, aniline, phenol, and much hydrogen cyanide.

A mixture of aniline and steam reacts at 650—700° to give a small quantity of phenol and also some carbazole. When a dilute solution of phenol in water is distilled through an iron tube heated at 930°, more than 90% of the substance suffers decomposition, naphthalene and gases being produced.

J. C. W.

The Volatile Reducing Substance in Cider Vinegar. R. W. BALCOM (J. Amer. Chem. Soc., 1917, 39, 309—315. Compare Farnsteiner, A., 1899, ii, 705; Pastureau, A., 1905, i, 559).—As a result of further experimental work, the author shows that the volatile reducing substances in cider vinegar consist largely,

if not wholly, of acetylmethylcarbinol, which is shown to be a normal constituent of this vinegar. W. G.

The Ethyl Hydrogen Sulphate Reaction. P. N. EVANS and J. M. ALBERTSON (*J. Amer. Chem. Soc.*, 1917, **39**, 456—461. Compare Claësson, A., 1879, 775).—A study of the reaction $\text{EtOH} + \text{H}_2\text{SO}_4 \rightarrow \text{EtHSO}_4 + \text{H}_2\text{O}$, with the view of determining its speed and degree of completeness, over a temperature range of 20—140°.

The results show that the reaction between equimolecular quantities of ethyl alcohol and sulphuric acid is about 58—60% complete when equilibrium is reached between 20° and 100°. The time required for equilibrium to be established varies from 150 minutes at 20° to 10 minutes at 70° and higher temperatures. The reaction is very slowly reversible if water is added, no difference in the acidity being noticeable after twenty-four hours at the ordinary temperature. From 70° upwards ether is formed with increasing rapidity, the acidity thus tending to rise again from its minimum with lapse of time. At the ordinary temperature there is a very slow formation of one or all of the three compounds, ethyl sulphate, isethionic acid, and ethionic acid, this being evidenced by a loss of 4% of the acidity in three weeks. W. G.

Heavy Oil of Wine. ROBERT KREMANN (*Monatsh.*, 1917, **38**, 53—62).—When 2.5 parts of concentrated sulphuric acid and 1 part of ethyl alcohol are distilled on a sand-bath, a product is obtained which settles into two layers. The lower layer is a yellow, oily liquid, formerly termed heavy oil of wine. This consists mainly of ethyl sulphate, but contains a small quantity (5%) of unsaturated hydrocarbons of the olefine series. An investigation of this oil is the subject of the present paper. On shaking with warm water, the whole of the ethyl sulphate is hydrolysed to ethyl hydrogen sulphate, which passes into solution, whereas the hydrocarbons remain undissolved. The hydrocarbon oil was collected and dried; it boiled at 280° and had $D=0.921$. On keeping, a solid, crystalline substance separated of $D=0.980$, m. p. 100°, b. p. 260°. This also is an olefine. Molecular weight determinations by the cryoscopic method (in acetic acid) and by the ebullioscopic method (in ether) showed that the liquid hydrocarbon has a mean molecular weight of 224, that is, $\text{C}_{16}\text{H}_{32}$, although in all probability a mixture of hydrocarbons is really present. The amount of the solid hydrocarbon was too small to allow of similar experiments being made. The author then carried out a series of hydrolysis experiments of the crude ethyl sulphate in aqueous, acid, and alkaline solutions, similar to those previously carried out with pure ethyl sulphate (A., 1907, ii, 157). The results obtained in these experiments led him to the conclusion that the crude ethyl sulphate prepared as above is not a mixture of ethyl sulphate and unsaturated hydrocarbons, but rather a mixture of ethyl sulphate and a compound of ethyl sulphate with the unsaturated hydrocarbons. J. F. S.

The Nitrogenous Hydrolysis Products of Heart Lecithin. C. G. MACARTHUR, F. G. NORBURY, and W. G. KARR (*J. Amer. Chem. Soc.*, 1917, **39**, 768—777).—Lecithin has been prepared from ox-heart and hydrolysed by boiling with 4½% hydrochloric acid. About 12% of its nitrogen is in a form insoluble in water after hydrolysis. Of the soluble nitrogen, about one half is in the form of choline and the other half in the form of aminoethyl alcohol. The very small amount of ammonia in the hydrolysed solution is probably a contamination. The amount of amino-acid nitrogen was also very small. Heart lecithin has practically the same composition as brain lecithin as far as its main constituents are concerned (compare Darrah and MacArthur, *A.*, 1916, i, 366), so that it is possible that the two lecithins are the same compound. Dehydration by means of acetone was found to be the most satisfactory method of preparing the tissue for work on the phosphatides. W. G.

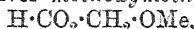
The Inositol Phosphoric Acids of Cottonseed Meal. J. B. RATHER (*J. Amer. Chem. Soc.*, 1917, **39**, 777—790. Compare A., 1913, i, 818).—From one sample of cottonseed meal an inositol-phosphoric acid has been isolated in the form of its strychnine salt, corresponding in composition and in the m. p. of its strychnine salt with inositol-triphosphoric acid (compare Clarke, T., 1914, **105**, 535). It does not appear, however, to be a constant constituent of cottonseed meal, since other samples of this meal similarly treated yielded an inositol-phosphoric acid corresponding in composition with inositol-pentaphosphoric acid or to the acid $C_{12}H_{41}O_{42}P_9$ previously reported (*loc. cit.*). The acid gives a strychnine salt, m. p. 220—222°. This same acid and its strychnine salt were also obtained by using the method described by Anderson (compare A., 1914, i, 641), by which he reported the isolation of inositol-hexaphosphoric acid. The silver salts of these acids were prepared and analysed. The author deems it best to ascribe the formula $C_6H_6(OH)(H_2PO_4)_5$ of the pentaphosphoric acid to this acid. W. G.

Catalytic Hydrogenation with Formic Acid, and Products of the Catalytic Condensation of Ordinary Acetone. ALPH. MAILHE and F. DE GODON (*Bull. Soc. chim.*, 1917, [iv], **21**, 61—64).—Formic acid in the presence of certain finely divided metals and metallic oxides is decomposed, giving carbon dioxide and hydrogen (compare Sabatier and Mailhe, A., 1912, i, 156). This reaction, copper and nickel being the catalysts, has been used for the hydrogenation of certain aromatic ketones at 300°. In this way, acetophenone, phenyl ethyl ketone, phenyl butyl ketone, phenyl propyl ketone, phenyl isopropyl ketone, benzyl isopropyl ketone, benzophenone, phenyl benzyl ketone, and *p*-tolyl benzyl ketone have readily been reduced to the corresponding hydrocarbons.

When this reaction was applied to acetone, the mixed vapours of acetone and formic acid being passed over finely divided nickel at 300°, the products were mesityl oxide, β -methylpentan- δ -one, a

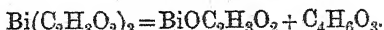
little valerone, and a more condensed product, b. p. 250°. The mesityl oxide is first formed from the acetone, and then undergoes partial or total hydrogenation. This preliminary condensation is also brought about by thoria at 410–420°. W. G.

Chloroethers. I. The Action of Chlorodimethyl Ether on Salts of Organic Acids. FRIEND E. CLARK, S. F. COX, and E. MACK (*J. Amer. Chem. Soc.*, 1917, **39**, 712–716. Compare Litterschied and Thimme, A., 1904, i, 963).—Methyl chloromethyl ether reacts with salts of the aliphatic acids to give methoxymethyl esters. Lead formate gives *methoxymethyl formate*,



b. p. 102–103°, D_0 1.1030, D_{15} 1.0366, D_{25} 1.0777, a clear liquid, with a slightly ethereal odour, burning with a blue flame, and reacting with water to give formic acid, formaldehyde, and methyl alcohol. Fused sodium or potassium acetate gives *methoxymethyl acetate*, b. p. 117–118°, D_0 1.0562, D_{15} 1.0358, D_{25} 1.0280, burning with a purple flame. Fused lead propionate gives *methoxymethyl propionate*, b. p. 133°, D_0 1.0137, D_{15} 0.9945, D_{25} 0.9872. It does not burn very readily, nor is it so easily decomposed with water as the two previous esters. Fused sodium butyrate yields *methoxymethyl butyrate*, b. p. 151–152°, D_0 0.9929, D_{15} 0.9747, D_{25} 0.9678. It is very difficultly inflammable and decomposes with water. The stability of the esters increases with the molecular weight. The introduction of a $\cdot\text{CH}_2\cdot$ group produces a rise of about 16° in the boiling point and a decrease in the density. W. G.

Bismuth Acetate. E. SALKOWSKI (*Biochem.-Zeitsch.*, 1917, **79**, 96–104).—The acetate was formed by dissolving the finely divided metal in a mixture of acetic acid and hydrogen peroxide, or by dissolving the hydroxide in acetic acid. A crystalline product, $\text{Bi}(\text{C}_2\text{H}_3\text{O}_2)_3$, was obtained, which is unstable and loses acetic acid on keeping in air, and more rapidly in a vacuum. If heated at 125°, it loses acetic anhydride rapidly and yields bismuthyl acetate:



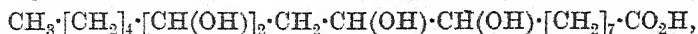
The bismuthyl salt, unlike the salt $\text{Bi}(\text{C}_2\text{H}_3\text{O}_2)_3$, is insoluble in water. S. B. S.

Studies in Steam Distillation. Propionic, Butyric, Valeric, and Hexoic Acids. H. DROOP RICHMOND (*Analyst*, 1917, **42**, 125. Compare A., 1908, i, 495, 754).—The acids were distilled under the conditions given previously (*loc. cit.*), and the results are given for the values x , y , and a ($x=1$ —water distilled %/100; y =acid distilled %/100; $a=\log.y/\log.x$). The value of a for the various acids was: propionic acid, 1.224; butyric acid, 2.00; valeric and isovaleric acids, 3.50. In the case of hexoic acid $a=3.71$, which was much lower than was expected. W. P. S.

The Preparation of Glycollic Acid. EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1917, **39**, 109–112).—In order to avoid the fractional crystallisation of calcium glycolate necessary in

Hölzer's method for preparing glycollic acid (compare A., 1884, 583) the author has modified the method. The chloroacetic acid (1 part) was heated on a water-bath with water (7 parts) and barium carbonate (2 parts) until no more carbon dioxide was evolved. More water (13 parts) was added and after a time a slight excess of barium carbonate, and the heating continued. The barium was then almost completely precipitated from the hot liquid by adding 95% of the calculated quantity of sulphuric acid, the barium sulphate filtered off, and the filtrate evaporated to a pale yellow syrup. The syrup was left to cool and inoculated with a crystal of glycollic acid and the whole set to a hard cake during the night. This was broken up and exposed to the air to allow the hydrochloric acid to evaporate, the crystals being finally recrystallised from water. Care must be taken during the evaporation to a syrup not to carry the process too far or a gelatinous anhydride separates out. W. G.

The Course of the Reaction which takes place when Higher Unsaturated Fatty Acids are Fused with Potassium Hydroxide. ALFRED ECKERT (*Monatsh.*, 1917, 38, 1—10).—With the object of examining the mechanism of the reaction between fused potassium hydroxide and the higher unsaturated fatty acids and also of testing the theory put forward to explain this reaction by Wagner (*Ber.*, 1888, 21, 3353), the author has examined the action of molten potassium hydroxide on several dihydroxy- and monohydroxy-fatty acids with the following results. Dihydroxystearic acid when fused with 6 times its weight of potassium hydroxide, 3 times its weight of water, and 3/5ths its weight of potassium chlorate at 200—220° for ten to twelve hours, yields pelargonic acid and azelaic acid. In the same way, dihydroxybehenic acid yields pelargonic acid and brassylic acid; satavic acid, .



yields azelaic acid, acetic acid, and hexoic acid; β -keto-stearic acid is practically unacted on. From these results the author draws the conclusion that dihydroxy-acids and monohydroxy-acids are not intermediate products in the decomposition of higher unsaturated fatty acids. Consequently, the probable course of the reaction is to be regarded as the direct shifting of the double linking to the end of the chain. J. F. S.

Fusion Diagram of the System, Methyl Oxalate-Water. ANTON SKRABAL (*Monatsh.*, 1917, 38, 25—29).—The freezing-point curve for methyl oxalate-water has been constructed. It is shown that methyl oxalate and water in the liquid state are soluble in one another to a limited extent. The ester has m. p. 53·5°, and on the addition of water this is lowered to 48°, at which temperature the ester crystallises out. The eutectic containing 4% of ester melts at -0·5°. At 48°, further addition of water has no effect on the freezing point until the mixture contains 84% of water, but over the whole of this range the molten substance consists of two phases. The effect of raising the temperature reduces this region only very

slightly. The values given are only to be regarded as limiting values, since the quantity of ester present is somewhat uncertain owing to the rapidity with which it is hydrolysed by water.

J. F. S.

Condensation Product of Cholic Acid with Formaldehyde.

SYNTHETIC PATENTS Co. (U.S. Pat., 1213261; from *J. Soc. Chem. Ind.*, 1917, 36, 403).—A compound of therapeutic value is produced by the combination of cholic acid and formaldehyde. It is a white powder, m. p. about 140°, soluble in alkali, alcohol, and glacial acetic acid.

H. W.

A Relation between the Chemical Constitution and the Optical Rotatory Power of the Phenylhydrazides of certain Acids of the Sugar Group. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1917, 39, 462—470).—Using Nef's figures (compare A., 1914, i, 490) for the specific rotatory powers of the phenylhydrazides of *d*-gluconic, *d*-gulonic, *d*-idonic, and *d*-galactonic acids, all of which contain α -, β -, γ -, and δ -asymmetric carbon atoms, the author calculates the rotation due to each of these atoms, and finds that the rotation due to the α -carbon atom is so very much larger than the values due to the other three atoms added together that the direction of rotation of the phenylhydrazide indicates the configuration of the hydroxyl group on the α -carbon atom. This is supported by the value for β -galaheptonic phenylhydrazide, the structure of which was settled by Peirce (compare A., 1916, i, 18). Further support is given by the specific rotatory powers of the phenylhydrazides of β -mannoheptonic acid (Peirce, *loc. cit.*), and of *d*-erythronic, *d*-threonic, and *d*-lyxonic acids (compare Nef, *loc. cit.*). In order to test the matter further, the author has prepared the following phenylhydrazides and measured their specific rotations in water: *d*-arabonic phenylhydrazide, $[\alpha]_D^{20} - 14.5^\circ$; *d*-mannonic phenylhydrazide, $[\alpha]_D^{20} - 8.1^\circ$; *l*-rhammonic phenylhydrazide, $[\alpha]_D^{20} + 17.2^\circ$; *d*- α -glucoheptonic phenylhydrazide, $[\alpha]_D^{20} + 9.3^\circ$; *d*- α -mannoheptonic phenylhydrazide, $[\alpha]_D^{20} + 21^\circ$; and *d*- α -galaheptonic phenylhydrazide, $[\alpha]_D^{20} + 8.7^\circ$. The rule holds for these six phenylhydrazides.

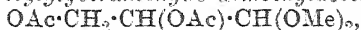
W. G.

Preparation of Acetaldehyde. UNION CARBIDE Co. (U.S. Pat., (A) 1213486 and (B) 1213487; from *J. Soc. Chem. Ind.*, 1917, 36, 403).—(A) Acetaldehyde is produced by passing acetylene into dilute sulphuric acid containing a mercury salt and a salt of a relatively weak acid which is not reduced under the working conditions, for example, a borate. The acetaldehyde may be distilled off simultaneously. (B) Acetaldehyde is produced by passing acetylene into a solution containing a mercury salt and an acid salt of a strong acid, for example, a bisulphate, but practically no hydrogen ions. The solution may also contain a salt of a relatively weak acid and the acetaldehyde may be distilled off simultaneously.

H. W.

The Sterical Relationships between Glyceraldehyde and Tartaric Acid. A. WOHL and FR. MOMBER (*Ber.*, 1917, 50, 455—462).—Dextrorotatory glyceraldehyde (A., 1915, i, 216) has been converted by the hydrogen cyanide synthesis into a trihydroxybutyric acid which yields *l*-tartaric acid on oxidation. It has therefore the same configuration as dextrose, and the designation "*d*-glyceraldehyde" will fortunately express both its optical activity and spatial relationships.

Some difficulty was experienced at first in effecting the hydrogen cyanide condensation, starting with glyceraldehyde dimethylacetal (*ibid.*). Assuming that the free aldehyde was peculiarly resistant to this action, the dibenzoate and diacetate of the acetal were prepared in the hope of hydrolysing these to the esters of the free aldehyde, but it was found that such a partial hydrolysis could not be effected. *Diacylglyceraldehyde dimethylacetal*,



has b. p. 128—129°/14 mm. Finally, it was realised that glyceraldehyde dimethylacetal is not completely hydrolysed by 0.1*N*-sulphuric acid in the cold, as was assumed. Warming for some time at 50° is necessary. *d*-Glyceraldehyde is now found to have a lower rotation than was originally stated, namely, $[\alpha]_D^{20} +13-14^\circ$.

After hydrolysing the acetal completely in this way, the addition of hydrogen cyanide can be effected in the presence of ammonia (HCN and NH₃, 1.5 mols. each). The nitrile may then be hydrolysed by barium hydroxide, and the brucine salt of the acid so formed may be obtained in clusters of needles, m. p. 204° (decomp.), $[\alpha]_D^{20} -29.9^\circ$. The salt is most probably a mixture of the salts of *l*-threonic and *d*-erythronic acids. The mixture of free acids may be oxidised by Fischer's method (A., 1896, i, 525) and the tartaric acid identified as the potassium salt.

Some useful suggestions are made for a simplification of the symbols for the aldoses. In reviewing the sterial relationships of the aldoses, it is only necessary, for example, to agree to consider the aldehyde group as being to the right of the formula and then to express in writing merely the groups on one side of the central chain, say, the lower side. Thus dextrose might be written
OH OH H OH. J. C. W.

Glyoxal. K. HESS and CL. UBRIG (*Ber.*, 1917, 50, 365—368).—Polymerised glyoxal can be depolymerised by boiling with anethole, phenetole, safrole, methyl nonyl ketone, benzaldehyde, and especially readily with acetic anhydride. With the last agent, it is observed that the solvent soon becomes greenish-yellow and that the vapour also contains monomeric glyoxal. After some hours, however, the solution becomes colourless again, and then *ethenyl tetra-acetate*, C₂H₂(OAc)₄, is deposited on cooling in cubes or rectangular prisms, m. p. 106—107°. This derivative of glyoxal is very reactive, and will undoubtedly serve in reactions involving the use of the dialdehyde. It reduces alkaline permanganate and ammoniacal silver oxide, and reacts with phenylhydrazine acetate

solution to form phenylglyoxalosazone, which crystallises in bundles of long, golden-yellow spikes from alcohol or reddish-brown prisms from 80% acetic acid, m. p. 169—170°. J. C. W.

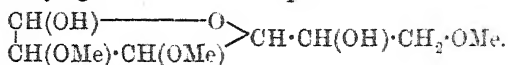
The Forms of *d*-Glucose and their Mutarotation. C. S. HUDSON and J. K. DALE (*J. Amer. Chem. Soc.*, 1917, **39**, 320—328).—The authors find that acetic acid of various concentrations is the most suitable solvent from which to crystallise glucose (compare Griffen and Nelson, A., 1915, i, 675). To prepare β -glucose from the purified glucose, 10 parts of the sugar are dissolved in 1 part of water on a water-bath, and to the solution 12 parts of glacial acetic acid heated to 100° are added. The whole is well mixed and removed from the water-bath, when crystallisation at once commences. After four such crystallisations, pure β -glucose is obtained. To obtain the α -form, 2 parts of the sugar are dissolved in 1 part of water and 4 parts of glacial acetic acid added, and the liquid set on one side for crystallisation to take place at the ordinary temperature.

The velocity coefficient, $(k_1 + k_2)$, at 25° of the mutarotation of β -glucose shows a slight increase with the concentration of the solution until a maximum rate is reached at 25 grams of the sugar in 100 c.c. of solution. In dilute solutions (under 10 grams in 100 c.c.), the rate is independent of the concentration.

The velocity coefficients for α - and β -glucose have been measured over a range of temperature from 0° to 40°, and are found to be the same for the two sugars at each temperature. They can be calculated from the formula $\log(k_1 + k_2) = C - A/T$, where C and A are constants. For an increase of 10° in temperature the rate increases 2.8 times. The acceleration of the hydrogen-ion catalysis of the mutarotation with rising temperature is the same as the acceleration by increased temperature of the rate of mutarotation in pure water. W. G.

Trimethyl Glucose [Dextrose Trimethyl Ether] from Cellulose. WILLIAM SMITH DENHAM and HILDA WOODHOUSE (*T.*, 1917, **111**, 244—249. Compare *T.*, 1913, **103**, 1735; 1914, **105**, 2357).—The most characteristic of the methylated glucoses obtained by the hydrolysis of methylated cellulose (*loc. cit.*) is a trimethyl glucose, and the probable structure of this compound is now discussed more particularly in the light of the discovery of γ -glucose and its derivatives. From a comparison of the properties of the trimethyl glucose with those of γ -glucose derivatives (Irvine, Fyfe, and Hogg, *T.*, 1915, **107**, 526), the conclusion is drawn that the former compound is not of the γ -glucose structure, but is to be regarded as derived from the butylene oxide structure. By a consideration of the various possible constitutions of the butylene oxide type for the trimethyl-glucose, and from the fact that by the cyanohydrin synthesis this substance is convertible into an acid which behaves as if partly lactonised, but which has in the process of lactonisation lost a

methyl group, the authors arrive at a decision that the structure of the trimethyl glucose is to be represented:



A compound of this constitution would by the cyanohydrin synthesis give rise to an acid which could form a lactone only by demethylation.

D. F. T.

The Preparation of Pure Crystalline Mannose and a Study of its Mutarotation. C. S. HUDSON and H. L. SAWYER (*J. Amer. Chem. Soc.*, 1917, **39**, 470—478).—A method is described for the preparation of crystalline β -mannose by the acid hydrolysis of vegetable ivory without the intermediate preparation of the phenylhydrazone (compare Fischer and Hirschberger, A., 1889, 480, 687). The vegetable ivory meal (150 grams) is slowly added in small quantities to a 75% solution of sulphuric acid (150 grams), the temperature not being allowed to rise above 40°. After twelve hours, the mixture is diluted with 2 litres of water and boiled for three hours under a reflux condenser. After cooling, the solution is neutralised with calcium hydroxide and filtered, and to the filtrate 0.5% of glacial acetic acid is added. The solution is decolorised with bone black, clarified with basic lead acetate solution, and the lead precipitated with hydrogen sulphide. The filtrate is evaporated to a thin syrup, diluted with alcohol, and filtered to remove calcium salts. Hydrogen sulphide is again passed through the alcoholic solution, which is finally filtered and evaporated to a viscous syrup, from which, on the addition of an equal volume of glacial acetic acid, β -mannose slowly crystallises. So prepared, it has D^{20} 1.539. The rate of mutarotation of this specimen in aqueous solution was measured at temperatures from 0° to 45°, and the reaction was found to be unimolecular (compare Pratolongo, *Rend. Inst. Lombardo*, 1912, **45**, 975), the increase in speed being 2.6 times for 10° rise in temperature. This rate of mutarotation is independent of the concentration for solutions less than 10% in strength. Above this, the rate increases with the concentration to a maximum, and then decreases. Hydrochloric acid acts as a catalyst for this reaction, the increase in rate being proportional to the increase in acidity within the range $N/1000$ to $N/10$. One drop of ammonium hydroxide brings about an equilibrium value for the rotation almost instantly.

W. G.

Pectin Substances, their Constitution and Importance. FELIX EHRLICH (*Chem. Zeit.*, 1917, **41**, 197—200).—The author, as the result of the investigation of the pectin substances obtained from sugar beet, has isolated a new substance, which stands in the same relation to d -galactose as does d -glycuronic acid to d -glucose. This substance he has named d -galacturonic acid. The residual cell material remaining after the removal of sugar from the sugar beet was used to prepare raw pectin. This material is shown to be

a mixture of two easily separable substances. The one, present only in small quantity, is a laevorotatory arabin ($[\alpha]_D = -74^\circ$ to -121°). The other is a calcium magnesium salt of pectic acid, which is a dextrorotatory ester acid. This substance can also be obtained from the skins of apricots and oranges. On treating the salt with alcohol and hydrochloric acid, the free pectic acid is obtained as a viscid, colourless jelly, which dries to a colourless powder. It is distinctly acid to litmus and phenolphthalein, dextrorotatory, $[\alpha]_D = +220^\circ$, and contains 9% of methoxyl groups. It gives the orcinol and resorcinol reactions for pentose, but its oxidation with nitric acid yields mucic acid, thus showing that it does not contain pentoses, but galactose. On heating pectic acid with 1% oxalic acid, it is hydrolysed, and yields *galactosegalacturonic acid*, a monobasic acid of the formula $C_{12}H_{20}O_{12} = C_6H_{12}O_6 + C_6H_{10}O_7 - H_2O$. This substance is a white, amorphous powder easily soluble in water and in alcohol; it forms calcium and barium salts, which are also soluble in water, but sparingly so in alcohol. It gives the orcinol and naphtharesorcinol reactions, and on oxidation with nitric acid yields mucic acid. Complete hydrolysis of pectic acid into *d*-galactose and *d*-galacturonic acid is effected by heating with oxalic acid under 2—3 atmospheres pressure at 130—140°. Pure galacturonic acid cannot, however, be isolated from the products of hydrolysis. If, on the other hand, pectic acid is treated with excess of cold sodium hydroxide solution, a white, flaky precipitate is deposited in a few seconds. This substance is an amorphous, white powder, which is easily soluble in dilute alkalis, and from the solution it is precipitated by acids. It has a rotatory power $[\alpha]_D = +270^\circ$, and is formed from pectic acid by the elimination of the methoxyl and galactose groups. The author regards it as being an anhydride of *d*-galacturonic acid, $4C_6H_{10}O_7 - 3H_2O = C_{24}H_{24}O_{25}$, formed in such a way that the separation of water takes place between the aldehyde and hydroxyl groups. This acid, *d*-tetragalacturonic acid, gives all the reactions of the pentoses and glycuronic acid, except that on oxidation it forms mucic acid and not saccharic acid. When heated for two hours under a pressure of 2—3 atmospheres with 1% oxalic acid solution, it breaks down into *d*-galacturonic acid. This substance has only been obtained as a syrup in alcohol or water; it is slightly dextrorotatory, and gives the orcinol, resorcinol, and phloroglucinol reactions. It reduces Fehling's solution cold, and on heating with hydrochloric acid it yields furfuraldehyde. It may be precipitated from solution by lead acetate, and with lime water or baryta water it yields basic salts. The normal calcium and barium salts are soluble in water or alcohol. It forms no crystallisable compounds with phenylhydrazine derivatives, and this serves to distinguish it from *d*-glycuronic acid. The cinchonine salt is the only crystalline derivative of this acid which has yet been obtained. This has the formula $C_6H_{10}O_7 \cdot C_{19}H_{22}ON_2$; it melts sharply at 158° and has $[\alpha]_D = +134^\circ$. Galacturonic acid is readily oxidised by bromine water to mucic acid, a reaction which serves to identify it in the

presence of galactose. Pectin substances obtained from a large number of fruits and vegetables have all been shown to be derivatives of this acid, so that the author regards it as playing an important part in the structure of plant material. As a result of the whole investigation, he draws the conclusion that the pectin of the cell membranes of plants is a calcium-magnesium salt of a complex *anhydro-arabino-galactose-methoxy-tetragalacturonic acid*. As to the method of linking of the various groups, there is no evidence on which to base definite conclusions, except that the arabinose group is weakly held in the molecule, whereas the galactose group is firmly held. The rest of the paper deals with possible uses of pectin substances as foods.

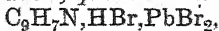
J. F. S.

Indirect Formation of Double Salts. VI. The Double Silver, Lead, Bismuth, Copper, and Mercurous Haloids of Substituted Ammonium Bases. RASIK LAL DATTA and JNANENDRA NATH SEN (*J. Amer. Chem. Soc.*, 1917, **39**, 750-759. Compare Datta and Ghosh, A., 1914, i. 729).—The salts described have been prepared by interaction of the metallic nitrate and the substituted ammonium haloid in concentrated aqueous solutions. In the case of the lower members of the substituted ammonium bromides, silver nitrate only gives a precipitate of silver bromide, the method failing even for tetramethyl- and tetraethyl-ammonium bromides. It is only the bromides of the heavy, heterocyclic bases that give double silver bromides. The following have been prepared, having the constitution $XBr, AgBr$:

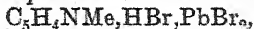
Pyridine silver bromide, a white, crystalline solid, m. p. 151° , readily decomposed by water; *quinoline silver bromide*, white, crystalline solid, m. p. 180° ; *isoquinoline silver bromide*, m. p. 127° ; *α -picoline silver bromide*, m. p. 157° . All these melted to yellow liquids and were decomposed by water.

The following double lead haloids were prepared:

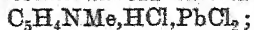
Tetraethylammonium lead iodide, $3NEt_4I, 2PbI_2$, m. p. 212° ; *tetrapropylammonium lead iodide*, NPr_4I, PbI_2 , m. p. 194° ; *p-tolyltrimethylammonium lead iodide*, $3NMe_3(C_6H_4)I, 2PbI_2$, a bright yellow solid, turning black when heated; *ethylquinolinium lead iodide*, C_9H_7NEtI, PbI_2 , m. p. 190° ; *tetramethylammonium lead bromide*, $3NMe_4Br, 2PbBr_2$; *tetraethylammonium lead bromide*; *pyridinium lead bromide*, $C_5H_5N, HBr, PbBr_2$, a white solid, turning yellow at 130° ; *quinolinium lead bromide*,



decomposing at 320° ; *α -picolinium lead bromide*,



m. p. $168-169^{\circ}$, to a viscid, black liquid; *pyridinium lead chloride*, $C_5H_5N, HCl, PbCl_2$; *α -picolinium lead chloride*,



quinolinium lead chloride, $C_9H_7N, HCl, PbCl_2$; *phenylbenzyl-diethyl ammonium lead chloride*, $C_7H_7-NEt_2, PhCl, PbCl_2$.

Double bismuth haloids have been prepared as follows:

Tetraethylammonium bismuth iodide, NEt_4I, BiI_3 ; *tetrapropyl ammonium bismuth iodide*, NPr_4I, BiI_3 ; *p-tolyltrimethylammonium*

bismuth iodide, $C_7H_7 \cdot NMe_3I, BiI_3$; ethylquinolinium bismuth iodide, $C_9H_7N, NEtI, BiI_3$; tetramethylammonium bismuth bromide; tetraethylammonium bismuth bromide; pyridinium bismuth bromide, a yellow solid, turning red suddenly at 210° ; quinolinium bismuth bromide. These bromides have the general formula $2XBr, BiBr_3$. Pyridinium bismuth chloride, $2C_5H_5N, HCl, BiCl_3$, m. p. 245° (decomp.); quinolinium bismuth chloride, $2C_9H_7N, HCl, BiCl_3$; phenylbenzyl-diethylammonium bismuth chloride, $C_7H_7 \cdot N, NEt_2, PhCl, BiCl_3$.

For the preparation of the double cuprous haloids, a hydrochloric acid solution of cuprous chloride was used. Tetrapropylammonium cuprous iodide, NPr_4I, CuI ; p-tolyltrimethylammonium cuprous iodide, $C_7H_7NMe_3I, CuI$; quinolinium cuprous iodide, C_9H_7N, HI, CuI ; methylquinolinium cuprous iodide (compare Kohn, A., 1912, i, 801); triethylsulphonium cuprous iodide, SEt_3I, CuI ; tetramethylammonium cuprous bromide, $NMe_4Br, 2CuBr$;

tetraethylammonium cuprous bromide, m. p. 130° ; phenylbenzyl-diethylammonium cuprous bromide, $C_7H_7 \cdot N, NEt_2, PhBr, CuBr$, a pale yellow, viscous oil, readily decomposing; pyridinium cuprous bromide, $C_5H_5N, HBr, CuBr$, unstable, yellow plates; quinolinium cuprous bromide, $C_9H_7N, HBr, CuBr$; isoquinolinium cuprous bromide; α -picolinium cuprous bromide, $C_5H_4NMe, HBr, CuBr$.

Double mercurous iodides were obtained with the heavily substituted ammonium bases. p-Tolyltrimethylammonium mercurous iodide, $C_7H_7 \cdot NMe_3I, HgI_2$; tetrapropylammonium mercurous iodide, $2NPr_4I, HgI_2$. W. G.

Preparation of Salts of Hexamethylenetetraminemethylhydroxide. K. H. SCHMITZ (D.R.-P., 295736; from *J. Soc. Chem. Ind.*, 1917, 36, 306).—Ammonia, formaldehyde, or one of its polymericides, and an acid or acid ion are heated for several hours and the product treated with a soluble dichromate; the resulting sparingly soluble chromate, $(C_6H_{12}N_4Me)_2Cr_2O_7$, is decomposed with barium hydroxide and the precipitated barium chromate filtered off. Alternatively, hexamethylenetetraminemethyl chloride, bromide, iodide, or thiocyanate is digested with silver oxide, the resulting solution of the free base is concentrated in a vacuum, neutralised by any desired inorganic or organic acid to form the corresponding salt, and the solution evaporated in a vacuum. The salts of this base have the property of liberating formaldehyde in alkaline solutions, which is not the case with hexamethylenetetramine salts, and have a therapeutic value. H. W.

Colloidal Ferric Ferricyanides. R. HALLER (*Kolloid Zeitsch.*, 1917, 20, 76—81).—By the interaction of aqueous solutions of ferric chloride and potassium ferricyanide, colloidal ferric ferricyanide is formed. The freshly formed colloid is highly disperse, but ultra-microscopic observations show that the particles undergo a gradual process of aggregation, and this leads ultimately to the separation of Prussian green. By the action of sodium hyposulphite on the

brown colloidal solution, a mixture of colloidal Prussian blue and Turnbull's blue is obtained. Further reduction yields colloidal Prussian white.

The actual result of the action of potassium ferricyanide on ferric chloride varies with the concentration of the aqueous solutions. If alcoholic solutions of ferric chloride and potassium ferricyanide are mixed together, ferric ferricyanide is obtained in the form of an unstable, gelatinous precipitate.

H. M. D.

The Preparation of Alkyloxyurea [Alkyloxyaminoformyl] Chlorides and their Relation to Esters of Carbon Dioxide Oxime, $RO\cdot N:C:O$. LAUDER WILLIAM JONES and LEONORA NEUFFER (*J. Amer. Chem. Soc.*, 1917, **39**, 652—659. Compare A., 1898, i, 172).—When phosphorus pentachloride is added slowly to α -benzyloxyurethane, hydrogen chloride and ethyl chloride are evolved and at 50° a violent reaction occurs giving a dark brown liquid. This, when distilled under reduced pressure, gives benzylidene chloride, the course of the reaction probably being:



the last compound decomposing or polymerising in part at 50°. α -*sec*-Butoxyurethane under similar conditions gives α -*sec*-butoxyaminoformyl chloride, a yellow oil, along with ethyl chloride and hydrogen chloride, the formation of the latter being due probably to the partial decomposition of the aminoformyl chloride (compare Gattermann and Schmidt, A., 1887, 358). *sec*-Butoxyethylaminoformyl chloride, a clear, colourless liquid, b. p. 80°/25 mm., is similarly prepared from the corresponding hydroxyurethane. Ethoxyethylaminoformyl chloride, b. p. 74—76°/25 mm., is similarly obtained. In some cases these aminoformyl chlorides are decomposed in the presence of water into hydroxylamine derivatives and carbon dioxide.

When carbonyl chloride is passed over hydroxylammonium chloride, the temperature being gradually raised to 100°, a clear liquid is formed and begins to distil, but explodes violently. With α -ethoxylammonium chloride at 200°, a clear liquid, $C_5H_9O_2NCl_2$, b. p. 190—200°, is obtained, and with α -benzyloxyammonium chloride a clear liquid, $C_8H_9O_2NCl_2$, b. p. 97·5—100°/49 mm., is obtained. With hydroxylamine at 45° carbonyl chloride gives a compound, a white, crystalline solid, m. p. 79·5—81° (decomp.), which gives a purple coloration with ferric chloride, and a green copper salt with copper acetate. The compound probably has the composition $HO\cdot NH\cdot COCl$. With ethoxylamine, carbonyl chloride gives at low temperatures a mixture of ethoxylammonium chloride and a compound, $C_5H_{13}O_3N_2Cl$, a clear, colourless oil.

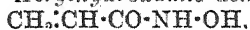
W. G.

Hydroxamic Acids Related to α -Hydroxy-acids and to Acrylic Acid, and a Study of their Rearrangements. LAUDER WILLIAM JONES and LEONORA NEUFFER (*J. Amer. Chem. Soc.*, 1917, **39**, 659—668. Compare A., 1898, i, 172).—Some new hydroxamic acids have been prepared by the action of free

hydroxylamine on the esters of certain acids, and the behaviour of these hydroxamic acids under the influence of heat and hydrolysing agents has been studied.

Ethyl propionate with hydroxylamine in methyl alcohol gives propionhydroxamic acid, $\text{CH}_3\text{Me}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$, m. p. $92.5-93^\circ$ (compare Miolati, A., 1892, 698). The copper, potassium, sodium, mercury, silver, and lead salts are described. The free acid gives a benzoyl derivative, $\text{CH}_3\text{Me}\cdot\text{CO}\cdot\text{NH}\cdot\text{O}\cdot\text{COPh}$, slender needles, m. p. $115-116^\circ$, which in turn yields sodium, potassium, and silver salts. The benzoyl derivative, when heated in a sealed tube in a water-bath with aqueous potassium hydroxide, decomposes, giving potassium benzoate, and on acidifying the solution with hydrochloric acid, ethylammonium chloride is also obtained. Propionhydroxamic acid also yields an acetyl derivative, glistening plates, m. p. $72.5-73^\circ$, which forms sodium, potassium, and silver salts.

Lacthydroxamic acid, $\text{HO}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$, a viscid, colourless oil, prepared as above, yields a benzoyl derivative, m. p. $124.5-126^\circ$, giving a potassium salt. The benzoyl derivative when heated with water on a water-bath for three hours gives carbon dioxide, ammonia, acetaldehyde, and *s*-dibenzoylcarbamide. Mandelhydroxamic acid, $\text{HO}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$, m. p. 143.3° , gives a benzoyl derivative, m. p. $101-102^\circ$, which very readily decomposes in contact with water, giving benzaldehyde and *s*-dibenzoylcarbamide. Acrylhydroxamic acid,

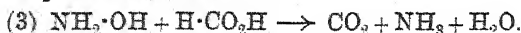
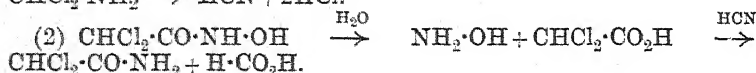
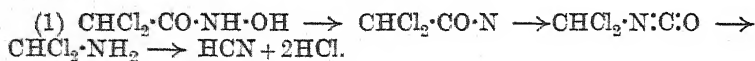


is a white, flaky solid, m. p. $115-116^\circ$.

W. G.

Dichloroacethydroxamic Acid and its Rearrangement, and Aminoacethydroxamic Acid. LAUDER WILLIAM JONES and M. CANNON SNEED (*J. Amer. Chem. Soc.*, 1917, **39**, 668-674).

—When hydroxylamine in alcoholic solution is added to an alcoholic solution of ethyl dichloroacetate at -10° , dichloroacethydroxamic acid, $\text{CHCl}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$, slender needles, m. p. $86-87^\circ$, is obtained. When heated at 145° , it is decomposed, giving carbon dioxide, hydrogen cyanide, hydrogen chloride, formic acid, ammonium chloride, dichloroacetamide, and dichloroacetic acid, the course of the decomposition being:



Further confirmation of this is obtained from the benzoyl derivative, b. p. $77-78^\circ$, which when heated decomposes, giving benzoic acid and a liquid having a sharp, carbimide-like odour, which when treated with water gives carbon dioxide, hydrogen chloride, and hydrogen cyanide. Attempts to prepare dichloromethylcarbimide by the interaction of sodium hydrazoate and dichloroacetyl

chloride only yielded an impure product, a colourless liquid, b. p. 85—90°, which had a sharp, penetrating odour, and was decomposed by water, giving carbon dioxide, hydrogen chloride, and hydrogen cyanide.

Ethyl trichloroacetate and hydroxylamine in alcoholic solution at -15° gave the *hydroxylammonium* salt of *trichloroacethydroxamic acid*, $\text{CCl}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{O}\cdot\text{NH}_2\cdot\text{OH}$, m. p. 72—73°. Ethyl glycololate and hydroxylamine gave *aminoacethydroxamic acid*, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$, m. p. 140° (decomp.). W. G.

The Thermal Decomposition of Benzene. J. E. ZANETTI and G. EGLOFF (*J. Ind. Eng. Chem.*, 1917, 9, 350—356).—A study of the thermal decomposition of benzene at temperatures varying from 500—800° at atmospheric pressure, the effect of varying the rate of flow of the benzene and the presence of catalysts being examined. The chief products of the decomposition are diphenyl, diphenylbenzenes, carbon, and a gas, no naphthalene being found in the decomposition products (compare Rittman, Byron, and Egloff, A., 1916, i, 132). The gas consisted of hydrogen saturated with benzene vapour, no acetylene being found. The formation of diphenyl begins at as low a temperature as 500°, the optimum temperature being 750°, above which diphenylbenzenes, as well as carbon and hydrogen, readily form. The slower rates of flow of the benzene are more favourable to the formation of diphenyl.

The catalysts examined were copper, iron, and nickel in the form of gauze. Iron and nickel favour the decomposition to carbon and hydrogen. Copper exerts no marked action except above 750°, when it accelerates the formation of carbon.

The thermal decomposition of benzene at atmospheric pressure takes place with the formation of condensation products, in which the benzene ring apparently remains intact, or with the complete breaking down to carbon and hydrogen without the formation of appreciable quantities of intermediate products, such as acetylene, ethylene, etc. W. G.

Halogenation. XV. Direct Iodination of Hydrocarbons by Means of Iodine and Nitric Acid. RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE (*J. Amer. Chem. Soc.*, 1917, 39, 435—441).—Iodine can be introduced directly into aromatic hydrocarbons by its action in the presence of nitric acid, the nitric acid being reduced to the lower oxides of nitrogen. In the case of the lower hydrocarbons, the chances of iodination are greater than those of nitration, but with the higher hydrocarbons the reverse is the case (compare Datta and Fernandes, A., 1916, i, 715). The nitric acid exerts to a small extent its hydrolysing influence, and with benzene a very small quantity of trinitrophenol can be isolated; but the nitric acid is added in small quantities, and thus its concentration is never sufficiently high for marked hydrolysis of the iodo-compound to occur. With the aliphatic hydrocarbons, however, the iodo-derivatives are hydrolysed as soon as they are

formed, but by careful working it is found possible to obtain small yields of the iodo-derivatives of some of the higher hydrocarbons. Using this method, benzene gave iodobenzene; toluene gave a mixture of *o*- and *p*-iodotoluenes; *o*-xylene gave 4-iodo-*o*-xylene; *m*-xylene gave 4-iodo-*m*-xylene; *p*-xylene gave 2-iodo-*p*-xylene; mesitylene gave iodomesitylene; ethylbenzene gave an iodoethylbenzene, b. p. 221—222°; cymene gave iodocymene; hexane gave a small yield of iodoheptane; thiophen with dilute nitric acid and iodine in the cold gave iodothiophen; naphthalene gave a mixture of iodo- and nitro-naphthalene; anthracene did not yield an iodo-derivative, but was oxidised to anthraquinone. W. G.

The Action of Sulphuric Acid on Certain Nitrocarbo-cyclic Compounds. I. The Action on Nitrobenzene.

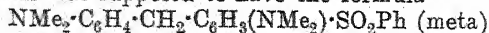
M. L. CROSSLEY and C. B. OGILVIE (*J. Amer. Chem. Soc.*, 1917, **39**, 117—122).—When nitrobenzene is heated with concentrated sulphuric acid at 195°, a vigorous action occurs, and from the product, after repeated extraction with boiling water, a black, melanin-like substance is obtained, which is practically insoluble in most organic solvents, but slightly soluble in pyridine, quinoline, and trimethylamine, giving reddish-purple solutions having a reddish-brown fluorescence. The aqueous extract on evaporation yields crystals of *p*-aminophenol-*o*-sulphonic acid; this gives an *anilide*, m. p. 98°, and on treatment with bromine in acetic acid solution, bromoanil, m. p. 300°.

When β -aminoanthraquinone, anthraquinone, or anthracene is separately added to the mixture of nitrobenzene and sulphuric acid, purplish-black reaction products are obtained which are similar to but not identical with the product obtained with nitrobenzene alone, but aminophenolsulphonic acid is not obtained. The black products in all cases dissolve in hot concentrated sodium hydroxide, and on the addition of sodium hyposulphite are reduced, giving dyes which dye cotton. The product from nitrobenzene dyes cotton a steel-grey. That from the aminoanthraquinone gives a brown vat, oxidising on cotton to a heliotrope. The anthraquinone product dyes cotton steel-grey, and the anthracene product dyes cotton brown. These dyes are not fast to boiling alkalis.

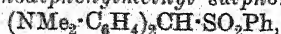
W. G.

The Reaction between Aromatic Sulphinic Acids and Di- and Tri-phenylcarbinols.

O. HINSBERG (*Ber.*, 1917, **50**, 468—473).—When equivalent quantities of benzenesulphinic acid and *pp'*-tetramethyldiaminobenzhydrol are mixed in dilute hydrochloric acid solution, a compound is formed which is colourless in benzene or acetone and deep blue in acetic acid solutions. Originally this was supposed to have the formula



(A., 1898, i, 140). It is now shown, however, that it is *phenyl pp'*-tetramethyldiaminodiphenylmethyl sulphone,



which exists in the quinonoid form, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Ph}$, in the coloured solutions. The evidence is to the effect that changes in the compound brought about at the central carbon atom necessitate the displacement of the sulphone residue. Thus, on reduction with zinc and dilute acid, the products are tetramethyldiaminodiphenylmethane and phenyl mercaptan; boiling with methyl-alcoholic sodium hydroxide causes hydrolysis to the hydrol methyl ether, m. p. 73° , and benzenesulphinic acid, whilst on warming with dimethylaniline and acetic acid, leuco-crystal-violet is produced.

Other sulphinic acids and hydrols react in the same way. Thus, Michler's hydrol condenses with β -anthraquinonesulphinic acid to form tetramethyldiaminodiphenylmethyl β -anthraquinonyl sulphone, $\text{C}_{14}\text{H}_9\text{O}_2 \cdot \text{SO}_2 \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, which crystallises in brownish-red leaflets, m. p. 220° , and gives deep blue solutions in acetic acid. Benzhydrol reacts with α -naphthalenesulphinic acid to form diphenylmethyl α -naphthyl sulphone, colourless needles, m. p. 183° , and with benzenesulphinic acid to give phenyl diphenylmethyl sulphone, m. p. 187° .

Triphenylcarbinol and α -naphthalenesulphinic acid give a strange product, m. p. 162° , which is free from sulphur. J. C. W.

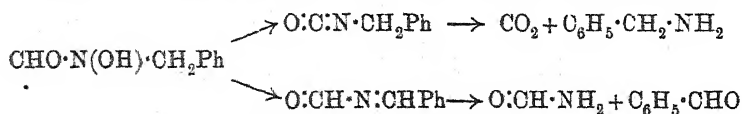
Diphenylbutadiene. J. M. JOHLIN (*J. Amer. Chem. Soc.*, 1917, **39**, 291—293).—The author considers that the hydrocarbon, $\text{C}_{16}\text{H}_{14}$, m. p. 49° , obtained from acetophenonepinacone by Thörner and Zincke (compare A., 1880, 646) by dehydration with acetic anhydride, is diphenylbutadiene. Three new methods are described for the preparation of acetophenonepinacone, namely: (1) reduction of acetophenone by magnesium in the presence of mercuric chloride; (2) conversion of diacetyl into its diphenylpinacone by means of magnesium phenyl bromide; (3) action of magnesium methyl iodide on benzil. Method (3) is the most convenient. W. G.

Normal Potassium Persulphate as a Reagent in Organic Chemistry. RASIK LAL DATTA and JNANENDRA NATH SEN (*J. Amer. Chem. Soc.*, 1917, **39**, 747—750. Compare Wolfenstein, A., 1904, i, 896).—With normal potassium persulphate, quinol is to a large extent oxidised in the cold to quinhydrone. Aniline gives a good yield of aniline-black. *o*-Toluidine gives a quantitative yield of *o*-toluidine-black. Acetanilide and benzanilide are oxidised to *p*-benzoquinone, the acid radicles being detached. Acetamide, propionamide, and butyramide are hydrolysed to the corresponding acids. Allyl alcohol is oxidised to acraldehyde and a viscous, oily substance, still under investigation. Benzamide does not give benzoic acid, but a complex acid, not yet characterised, is produced. Cinnamic acid, pinene, and limonene give yellow to brown products of high molecular weight. With the aromatic amines and diamines, various dyes are produced, which are being investigated. W. G.

Preparation of Diphenylamine. B. J. FLÜRSCHHEIM (U.S. Pat., 1212928; from *J. Soc. Chem. Ind.*, 1917, **36**, 382).—Aniline is heated with ferric chloride, finely divided copper, and iodine.

H. W.

β -Benzylformhydroxamic Acid. LAUDER WILLIAM JONES and M. CANNON SNEED (*J. Amer. Chem. Soc.*, 1917, **39**, 674—679).—A solution of β -benzylhydroxylamine in ethyl formate kept for fourteen days at the ordinary temperature yielded β -benzylformhydroxamic acid, $\text{CHO}\cdot\text{N}(\text{C}_6\text{H}_5)\cdot\text{OH}$, long needles, m. p. 49—50°, giving a greyish-blue copper salt. The acid, when digested for two hours on a water-bath with an excess of a solution of dry hydrogen chloride in glacial acetic acid, underwent intramolecular oxidation in two directions, giving, on the one hand, carbon dioxide and benzylamine, and on the other hand formamide and benzaldehyde:



When distilled with phosphoric oxide, the acid gave benzylcarbimide, which, with aniline, yielded phenylbenzylcarbimide. W. G.

Nitrosoarylhydroxylamines. V. Internally Complex Metallic Salts. OSKAR BAUDISCH and ROSE FÜRST (*Ber.*, 1917, **50**, 324—327. Compare A., 1916, i, 386, 387, 388, 389).—The metallic salts of nitrosophenylhydroxylamine (cupferron) and α - and β -nitrosonaphthylhydroxylamine exhibit many differences in solubility which might be turned to account in analytical practice. An account of some of these solubilities is given.

For the preparation of the new β -naphthyl compound, β -nitro-naphthalene is reduced by means of ammonium sulphide to β -naphthylhydroxylamine, silvery leaflets, m. p. 126°, and this is treated in ethereal solution with amyl nitrite in the presence of ammonia, when the ammonium salt, $\text{C}_{10}\text{H}_7\cdot\text{N}(\text{NO})\cdot\text{ONH}_4$, separates in pearly leaflets, m. p. 159—160°. Free β -nitrosonaphthylhydroxylamine is obtained from this salt by means of metaphosphoric acid, in white needles, m. p. 88—92°. It is much more stable than the α -naphthyl compound (A., 1913, ii, 39), and gives precipitates with the merest traces of calcium or magnesium salts. The copper salt is pale bluish-green and the ferric salt is yellowish-brown.

If wool is steeped in a solution of ammonium β -nitrosonaphthylhydroxylamine and then exposed to a light, it becomes deep red, owing to the formation of α -hydroxy- β -azonaphthalene, which can be extracted from the wool by means of boiling alcohol and obtained in ruby-red needles, m. p. 234°. J. C. W.

Nitrosoarylhydroxylamines. VI. Internally Complex Metallic Salts. OSKAR BAUDISCH and NIKOLAUS KARZEFF (*Ber.*, 1917, **50**, 328—330).—For comparison with o -nitrosohydroxylamino-

phenol and its *p*-toluenesulphonate, the corresponding derivatives of *p*-nitrosophenol have been prepared (see A., 1912, i, 441).

p-Nitrophenyl *p*-toluenesulphonate is reduced by means of ammonium sulphide to *p*-hydroxylaminophenyl *p*-toluenesulphonate, m. p. 104.3°, and this is converted into *p*-nitrosohydroxylaminophenyl *p*-toluenesulphonate, $C_6H_4 \cdot SO_2 \cdot O \cdot C_6H_4 \cdot N(NO) \cdot OH$, white needles, m. p. 84.2°. Like the ortho-compound, this acid forms typical, internally-complex salts which are readily soluble in organic media, but differ from the salts of the ortho-acid in being soluble in an excess of hydrochloric acid. The ammonium salt, m. p. 132°, is precipitated when amyl nitrite is added to the above hydroxylamino-compound in ether saturated with ammonia; the ferric salt crystallises from ether in brown needles.

The ammonium salt can be hydrolysed by silver oxide to *p*-nitrosophenyl *p*-toluenesulphonate, which, unlike the ortho-compound, exists in only one form, white needles, m. p. 143°. The same salt is hydrolysed by sodium hydroxide, on the other hand, to *p*-nitrosohydroxylaminophenyl *p*-toluenesulphonate, $OH \cdot C_6H_4 \cdot N(NO) \cdot OH$, which crystallises in leaflets, decomp. 70–100°, and forms a white ammonium salt, m. p. 131–132°.

J. C. W.

Nitrosoarylhydroxylamines. VII. Internally Complex Metallic Salts. Note on Mordant Dyes. OSKAR BAUDISCH and FRANZ KLAUS (*Ber.*, 1917, 50, 330–331).—*m*-Nitrophenol has been converted by the usual methods into the ammonium salt of *p*-nitroso-*m*-hydroxylaminophenylhydroxylamine, and the solubilities of the copper and cobalt salts of this acid have been compared with those of the salts of the corresponding *o*-hydroxy- and *p*-hydroxy-acids (A., 1912, i, 441, and preceding abstract). The salts in the ortho-series are very soluble in water, organic solvents, ammonia, or pyridine, and readily lose H and NO, whilst the salts in the para-series are insoluble except in ammonia or pyridine and are stable. The salts of the meta-acid take an intermediate position.

This influence of substituents on internally-complex groups is akin to the influence of substituents in *o*-hydroxyazo-compounds on their value as mordant dyes.

J. C. W.

Preparation of Phenol and Other Substances. J. W. AYLSWORTH, A. M. AYLSWORTH, and THE SAVINGS, INVESTMENTS, AND TRUSTS CO., EXORS. (U.S. Pat., 1213142; from *J. Soc. Chem. Ind.*, 1917, 36, 382).—Phenol is obtained by heating a mixture of chlorobenzene and alkali hydroxide solution, under pressure higher than that of the vapour tension of the mixture, at about 300°. Chloride and phenoxide are produced, and phenol is liberated from the latter by the action of acid. Where sodium hydroxide is used, the proportions are approximately: chlorobenzene (1 mol.), alkali hydroxide (2–3 mols.), and water (20 mols.).

H. W.

Electrolytic Oxidation of Cresols [Preparation of Salicylic Acid]. U. POMILIO (Brit. Pat., 103709; from *J. Soc. Chem. Ind.*, 1917, **36**, 382).—In the oxidation of cresols for the production of the corresponding hydroxy-acids or their salts, an electric current of 5—8 amperes per sq. decm. is passed through a fused mixture of the cresol and alkali hydroxide at 200—270°, using electrodes of nickel, nickel-steel, iron, etc. For example, in the production of salicylic acid, a mixture of sodium hydroxide (3—5 parts) and water (1 part) at 110—120° is treated with *o*-cresol (85—95%, 1 part), added in small quantities at a time; the mixture is then heated at 240—250° and a current of 5—8 amperes per sq. decm. at the anode passed through. H. W.

Halogenation. XVI. Iodination by Means of Nitrogen Iodide or by Means of Iodine in the Presence of Ammonia.

RASIK LAL DATTA and NOGENDRA PRASAD (*J. Amer. Chem. Soc.*, 1917, **39**, 441—456).—It is found that the phenols and the nitrophenols can be satisfactorily iodinated by means of nitrogen iodide or by a solution of iodine in potassium iodide in conjunction with strong ammonium hydroxide solution. With the latter reagent the iodonitrophenols, as formed, give ammonium salts of varying degree of stability, which cannot be prepared once the iodonitrophenol has been isolated. In all cases the yields were quantitative. Phenol gave tri-iodophenol; *o*-cresol gave di-iodo-*o*-cresol; *m*-cresol gave tri-iodo-*m*-cresol; *p*-cresol gave 3:5-di-iodo-*p*-cresol; thymol gave 6-iodothymol; and *p*-5-xyleneol gave a *moniodo*-derivative which was not characterised. *o*-Nitrophenol gave the ammonium salt, m. p. 210° (decomp.), of 2:4-di-iodo-6-nitrophenol; *m*-nitrophenol gave the unstable ammonium salt, m. p. 165—170°, of 2-iodo-3-nitrophenol; *p*-nitrophenol gave 2:6-di-iodo-4-nitrophenol, no ammonium salt being isolated; 3-nitro-*p*-cresol gave 5-iodo-3-nitro-*p*-cresol, yellow needles, m. p. 83.5°, isolated first as its ammonium salt, orange-red needles, m. p. 195—200°; phenolphthalein gave tetraiodophenolphthalein.

The phenolic acids could be less readily iodinated by iodine and ammonia than the phenols and nitrophenols, as, in addition to iodo- or di-iodo-derivatives, secondary products of a complex character were always formed. Salicylic acid gave 5-iodosalicylic acid and a pink compound; *m*-hydroxybenzoic acid gave 6-iodo-*m*-hydroxybenzoic acid; *p*-hydroxybenzoic acid gave 3:5-di-iodo-*p*-hydroxybenzoic acid and a compound not yet characterised; *p*-hydroxyphenylarsinic acid gave an iodo-derivative, $\text{HO}\cdot\text{C}_6\text{H}_3\text{I}\cdot\text{AsO}(\text{OH})_2$, needles, m. p. 158°, which when boiled with water gave a pink compound, m. p. 230—240°.

Dimethylpyrone in the presence of iodine and ammonia gave a shining, micaceous substance, which was ultimately converted into di-iodolutidone, $\text{CO} \begin{smallmatrix} \text{OI:OMe} \\ \text{OI:OMe} \end{smallmatrix} \text{NH}$, m. p. 230—235°, giving a hydrochloride, yellow needles, and iodoform. Pyrrole gave a quantitative yield of tetraiodopyrrole, and on this is based a simple

volumetric method for the estimation of pyrrole, using an $N/2$ -solution of iodine in potassium iodide.

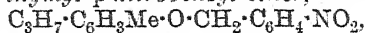
Acetylene acting on nitrogen iodide under water gives a quantitative yield of tetraiodoethylene, whilst phenylacetylene under similar conditions gives tri-iodostyrene, m. p. 108°.

In two cases nitrogen iodide acted as an oxidising agent as with quinol it gave quinhedrone, and with benzaldehyde it gave benzoic acid.

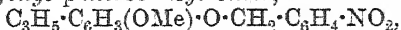
Iodoform is formed as a product of the systematic action of nitrogen iodide on the ketones (compare Chattaway, T., 1913, 103, 1986), but if the reaction is carried out in concentrated solutions and at lower temperatures iodo-ketones are apparently formed, although none have yet been isolated. Thus acetone, methyl ethyl ketone, diethyl ketone, acetylacetone, acetylmethyl propyl ketone, acetylmethyl hexyl ketone, acetoxime, acetophenoneoxime, malonic ester, and acetoacetic ester all gave iodoform in the presence of nitrogen iodide, although with the first five there were strong indications of the formation of iodo-ketones. Diethylamine and triethylamine also gave iodoform with iodine and ammonia, as also did mesityl oxide. Iodine in the presence of ammonia has no action on ethyl and propyl alcohols.

W. G.

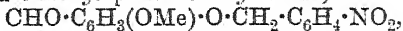
The Identification of Phenols. E. EMMET REID (*J. Amer. Chem. Soc.*, 1917, 39, 304—309).—It is found that *p*-nitrobenzyl bromide readily reacts with the sodium or potassium phenoxides, giving ethers that are generally crystalline solids, and can be used as a means of identifying the phenols. The reaction is carried out in alcoholic solution, the mixture being heated on a water-bath under a reflux for one hour. The following ethers were prepared: Phenyl *p*-nitrobenzyl ether, m. p. 91° (compare Kumpf, A., 1884, 1005); *o*-tolyl *p*-nitrobenzyl ether, $C_6H_4Me \cdot O \cdot CH_2 \cdot C_6H_4 \cdot NO_2$, m. p. 89·7°; *m*-tolyl *p*-nitrobenzyl ether, m. p. 51°; *p*-tolyl *p*-nitrobenzyl ether, m. p. 88°; *thymyl p*-nitrobenzyl ether,



m. p. 85·5°; *eugenyl p*-nitrobenzyl ether,



m. p. 53·6°; and *vanillyl p*-nitrobenzyl ether,



m. p. 124·5°. All these ethers can be crystallised from alcohol.

W. G.

The Identification of Acids. E. EMMET REID (*J. Amer. Chem. Soc.*, 1917, 39, 124—136).—*p*-Nitrobenzyl bromide is a convenient reagent for the identification of acids. It readily forms esters of the acids when boiled in dilute alcoholic solution with the alkali salts of the acids. The esters can, in most cases, be readily purified by crystallisation from dilute alcohol. The following esters have been prepared:

p-Nitrobenzyl formate, m. p. 31°; acetate, m. p. 78° (compare Wachendorf, A., 1877, i, 207); propionate, m. p. 31°; butyrate, m. p. 35°; benzoate, m. p. 89°; *o*-toluate, m. p. 90·7°; *o*-nitro-

benzoate, m. p. 111.8°; *o-chlorobenzoate*, m. p. 106°; *anthranilate*, m. p. 205—210° (decomp.); *p-bromobenzoate*, m. p. 139.5°; 2:4-*dinitrobenzoate*, m. p. 142°; *phenylpropionate*, m. p. 83°; *thiocyanate*, m. p. 85° (compare Henry, *Ber.*, 1869, 2, 638); *oxalate*, m. p. 204° (compare Beilstein and Kuhlberg, *Annalen*, 1868, 147, 340); *malonate*, m. p. 85.5°; *tartrate*, m. p. 163°; *citrate*, m. p. 102°.

Esters were made from salts of *isobutyric*, *isovaleric*, *octoic*, *lactic*, and α -*hydroxybutyric* acids, but the products were all oils which could not be induced to solidify. Attempts to prepare *p*-nitrobenzyl nitrite from potassium nitrite only gave a very small yield of a compound having a high melting point, and this was not proceeded with. With benzoic acid and its substitution products the yields are practically quantitative. The lower aliphatic monobasic acids also give good yields, but the yields from the polybasic acids are poor. W. G.

The Identification of Acids. II. J. A. LYMAN and E. EMMET REID (*J. Amer. Chem. Soc.*, 1917, 39, 701—711. Compare preceding abstract).—*p*-Nitrobenzyl esters of a number of other acids have been prepared, *p*-nitrobenzyl chloride and iodide being used in some cases in place of the bromide. With the dibasic acids, attempts to prepare the mono- as well as the di-ester failed in all cases except one, namely, malic acid. The following esters are described: *p*-nitrobenzyl *phenylacetate*, m. p. 65°; *cinnamate*, m. p. 116.7°; β -*phenylpropionate*, m. p. 36.3°; *hippurate*, m. p. 136°; *m-toluate*, m. p. 86.6°; *salicylate*, m. p. 96.3°; *m-hydroxybenzoate*, m. p. 106.1°; *p-hydroxybenzoate*, m. p. 198.5°; *m-amino-benzoate*, m. p. 198.3°; *p-aminobenzoate*, m. p. above 250°; *ethylmalonate*, $\text{CHEt}(\text{CO}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2)_2$, m. p. 75.2°; *dimethylmalonate*, m. p. 83.6°; *methyl ethylmalonate*, m. p. 65.6°; *isopropylmalonate*, m. p. 81.4°; *diethylmalonate*, m. p. 91.2°; *allylmalonate*, m. p. 46°; *dipropylmalonate*, m. p. 118.5°; *benzylmalonate*, m. p. 119.5°; *succinate*, m. p. 88.4°; *bromosuccinate*, m. p. 147.1°; *dibromosuccinate*, m. p. 168.5°; *maleate*, m. p. 89.3°; *fumarate*, m. p. 150.8°; *sebacate*, m. p. 72.6°; *malates*,

$\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, m. p. 87.2°, and $\text{C}_6\text{H}_4\text{O}(\text{CO}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, m. p. 124.5°; *racemate*, m. p. 147.6°; *phthalate*, m. p. 155.5°; *isophthalate*, m. p. above 250°. The esters described above from dibasic acids are always the normal esters, except in the case of the malates. Esters could not be obtained with *lævulic* and *mucic* acids. W. G.

The Transformation of Nitriles into Amides by Hydrogen Peroxide. L. McMASTER and F. B. LANGRECK (*J. Amer. Chem. Soc.*, 1917, 39, 103—109. Compare Dubsy, A., 1916, i, 550).—By the action of hydrogen peroxide in a slightly alkaline medium, nine amides have been prepared in a pure state and with good yields from the corresponding nitriles. The amides thus prepared are *benzamide*, *m*-nitrobenzamide, *o*-toluamide, *p*-toluamide, α -naphthoamide, β -naphthoamide, *terephthalamide*, *trichloroacetamide*, and *isohexoamide*. The authors have used more concen-

trated solutions of hydrogen peroxide than are usually employed, using in some cases a 20% solution, and thus succeeded in hydrolysing certain nitriles which had previously resisted the action of hydrogen peroxide (compare Deinert, A., 1896, i, 149). W. G.

Isomerisation, by Migration of the Double Linking, in the Ethylenic Acids. Phenyl- Δ^{α} -crotonic Acid, $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$. J. BOUGAULT (*Compt. rend.*, 1917, 164, 633—636. Compare A., 1911, i, 202).—Phenyl- Δ^{α} -crotonic acid can be readily prepared from the liquid acid obtained in the reduction of α -iodophenylcrotonic acid with zinc and acetic acid (compare A., 1916, i, 817) by simply heating it with dilute hydrochloric acid. This Δ^{α} -acid is almost completely converted into its Δ^{β} -isomeride by warming it on a water-bath for three hours with dilute aqueous sodium hydroxide. The direction of this isomerisation is considered to be due to the presence of the electronegative phenyl group (compare Charon, *Rev. gen. des Sci.*, 1904, 15, 447). W. G.

The Relationships between Keto- and Enol Forms in the Case in which the Enolisation is caused by a Positive β -Influence. L. RÜGHEIMER (*Ber.*, 1917, 50, 396—401).—The question of the equilibrium between the two forms of ethyl β -benzyliminobutyrate has been investigated (compare A., 1916, i, 383).

The purest ketonic modification, $\text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, obtained so far was prepared by the addition of benzylamine to an ethereal solution of ethyl acetoacetate at -5° , followed by crystallisation from cold ether, in which the enol is freely soluble. It forms elongated tablets, and in a bath previously warmed to 75° melts at $88.5\text{--}94.5^{\circ}$. The purest enolic modification, $\text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{OEt}$, is obtained by distilling the compound under reduced pressure (b. p. $189^{\circ}/20\text{ mm.}$) and collecting the product in the dark. A fresh specimen has m. p. $19\text{--}22^{\circ}$, although the fusion is still somewhat turbid at 25° .

The ketonic form is permanent at the ordinary temperature if protected from catalytic influences, for example, from dust, but if heated, it suffers partial change into the enol, the m. p. becoming lower after each fusion. Conversely, the enol changes partly into the ketone at $20\text{--}23^{\circ}$, even in the dark, and therefore a fresh distillate is found to be solid after keeping for a few days.

It is thus established that equilibrium exists between the two forms in the liquid state. At higher temperatures the enolic form is favoured, whilst at lower temperatures the ketonic form is more stable, and in consequence of its small solubility a very complete transformation may take place. At about 53° it is possible to maintain both forms, liquid enol and solid ketone, together for some time. J. C. W.

The Action of the Tolythiocarbimides on Sodiophenylacetylene. DAVID E. WORRALL (*J. Amer. Chem. Soc.*, 1917, 39, 697—701).—The tolythiocarbimides condense with sodiophenyl-

acetylene, yielding on addition of acid thiotoluidides. Sodio-phenylacetylene and *p*-tolylthiocarbimide react in ethereal solution to form *thiophenylpropiol-p-toluidide*, $\text{CPh:C}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, yellow needles, m. p. 111—113° (decomp.), giving a *sodium* salt, colourless needles, which is unstable in water. The thiotoluidide when heated in ethereal solution with a few drops of aqueous sodium hydroxide polymerises, giving *bis-thiophenylpropiol-p-toluidide*, red plates, softening at 200°, but having no definite melting point. With phenylhydrazine in alcoholic solution the thiotoluidide, m. p. 111—113°, gives off hydrogen sulphide, and a brick-red precipitate is formed, but no crystalline product could be isolated (compare Moureu and Brachin, A., 1903, i. 581; 1904, i. 95). With hydroxylamine the thiotoluidide gives 3-*p-toluidino-5-phenylisooxazole*, white plates, m. p. 141.5°, hydrogen sulphide being evolved.

Thiophenylpropiol-m-toluidide, yellow needles, m. p. 118—120° (decomp.), was only obtained in small quantities, but qualitative tests indicate that it reacts with phenylhydrazine and with hydroxylamine, hydrogen sulphide being liberated.

Thiophenylpropiol-o-toluidide could only be obtained as a dark-coloured oil, giving a *sodium* salt, colourless plates. W. G.

Nitration of Isomeric Acetylamino-methoxybenzoic Acids.

JOHN LIONEL SIMONSEN and MADYAR GOPALA RAU (T., 1917, 111, 220—236. Compare Gibson, Simonsen, and Rau, this vol., i. 203). —An extension of the earlier nitration experiments to the simpler acids—3-acetylamino-2-methoxybenzoic acid, 5-acetylamino-2-methoxybenzoic acid, 4-acetylamino-3-methoxybenzoic acid, and 3-acetylamino-4-methoxybenzoic acid. The previous observation that the directing influence of a methoxy-group is much intensified by the juxtaposition of the acetylamino-group, in contrast with the opposite effect of a negative group, such as carboxyl, is, on the whole, borne out by the new results.

3-Acetylamino-2-methoxybenzoic acid, prepared through its parent amino-compound from 3-nitro-2-methoxybenzoic acid, when nitrated yielded the 4-nitro-, 5-nitro-, and 6-nitro-derivatives to the extent of 10, 42.8, and 40% respectively; the last-named product was further converted into 6-nitro-2-methoxybenzoic acid by the diazo-reaction.

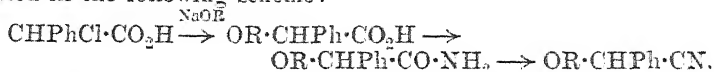
5-Acetylamino-2-methoxybenzoic acid, obtained similarly from 5-nitro-2-methoxybenzoic acid, yielded the 4-nitro-, 6-nitro-, and 3-nitro-derivatives to the extent of 68, 7, and 22% respectively; 4-nitro-2-methoxybenzoic acid was obtained from the first of these products by diazotisation.

4-Acetylamino-3-methoxybenzoic acid, prepared in a similar manner to its isomerides, yielded its 6-nitro-derivative as the only simple nitration product.

3-Acetylamino-4-methoxybenzoic acid, prepared in the general manner, gave its 6-nitro-derivative as the only simple nitration product; this, by hydrolysis and diazotisation, was converted into 2-nitro-4-methoxybenzoic acid.

For experimental details and the description of the various compounds obtained in the preparation and nitration of the acetyl-amino-acids the original should be consulted. D. F. T.

Alkyl Ethers of Benzaldehydecyanohydrin. I. K. HESS and K. DORNER (*Ber.*, 1917, 50, 390—394).—Alkyl ethers of benzaldehydecyanohydrin have not hitherto been described, although they are constitutionally related to amygdalin. A method for the preparation of such ethers has now been developed, which is indicated in the following scheme:



The methyl and ethyl compounds are described in this communication.

α -Chlorophenylacetic acid is boiled with sodium methoxide solution and so converted into α -methoxyphenylacetic acid, m. p. 70—71°, which is accompanied by a troublesome by-product, m. p. 91°, thus rendering this method less suitable than the usual one for obtaining the ether of mandelic acid. α -Methoxyphenylacetyl chloride has b. p. 119—121°/26 mm., and the amide crystallises in pearly plates, m. p. 112—114°, being best obtained from the methyl ester. α -Methoxyphenylacetoneitrile, $\text{OMe} \cdot \text{CHPh} \cdot \text{CN}$, is obtained by heating the amide with pure thionyl chloride. It is a very stable, refractive, mobile oil, b. p. 116—118°/14 mm.

α -Ethoxyphenylacetamide forms pearly needles, m. p. 93—94°, and α -ethoxyphenylacetoneitrile has b. p. 122—124°/16 mm. Methyl α -ethoxyphenylacetate has b. p. 127—129°/14—15 mm. J. C. W.

The Synthesis of Aryl-substituted Fatty Acids. FERDINAND MAUTNER (*J. pr. Chem.*, 1917, [ii], 95, 55—62. Compare A., 1910, i, 115).—The author has extended to other aldehydes his method for the preparation of arylacetic acids.

[With (FRL.) ELSA MIKA.]— α -Naphthaldehyde was, in the general manner, converted into the corresponding *azlactone*, $\text{C}_{20}\text{H}_{18}\text{O}_2\text{N}$, yellow needles, m. p. 170—171°, by heating with hippuric acid, acetic anhydride, and sodium acetate; this product, on successive hydrolysis with sodium hydroxide solution and oxidation of the resulting alkaline solution with hydrogen peroxide, yielded α -naphthylacetic acid.

In an analogous manner, 2-methoxy-1-naphthaldehyde was converted into the *azlactone*, $\text{C}_{21}\text{H}_{15}\text{O}_3\text{N}$, yellow needles, m. p. 178—179°, which on hydrolysis with sodium hydroxide solution followed by prolonged distillation with steam gave 2-methoxy-1-methylnaphthalene and 2-methoxy-1-naphthylpyruvic acid, $\text{C}_{14}\text{H}_{12}\text{O}_4$, m. p. 119—120°; oxidation of the latter in acetic acid solution with hydrogen peroxide produced 2-methoxy-1-naphthylacetic acid, $\text{C}_{13}\text{H}_{12}\text{O}_3$, m. p. 210—211°. Similarly, 4-methoxy-1-naphthaldehyde yielded an *azlactone*, $\text{C}_{21}\text{H}_{15}\text{O}_3\text{N}$, reddish-yellow needles, m. p. 189—190°, which by hydrolysis and subsequent oxidation of the resulting alkaline solution was converted into 4-methoxy-1-naphthylacetic acid, $\text{C}_{13}\text{H}_{12}\text{O}_3$, colourless needles, m. p. 144—145°.

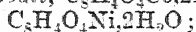
By the same general reaction *o*-chlorobenzaldehyde and *m*-bromobenzaldehyde were made to yield the corresponding *azlactones*, $C_{16}H_{10}O_2NCl$, yellow needles, m. p. 158—159°, and $C_{16}H_{10}O_2NBr$, m. p. 156—157° respectively, which were further convertible into *o*-chlorophenylacetic acid and *m*-bromophenylacetic acid respectively.

D. F. T.

The Salts of Phthalic Acid. JOHN B. EKELEY and CLIFFORD BANTA (*J. Amer. Chem. Soc.*, 1917, **39**, 759—768).—A study of the effect of heat on calcium phthalate under varying conditions of temperature and pressure, and an account of the preparation of a number of new salts of phthalic acid.

Calcium phthalate when heated either under reduced pressure at low temperatures, or at higher temperatures under pressure, only gave traces of anthraquinone (compare Panaotovic, A., 1884, 1039). The main products were resinous matter, phthalic anhydride, and benzophenone. Sodium phthalate when heated at 80° under a pressure of 13 mm. gave benzophenone as its principal product. Lead phthalate gave off water and carbon dioxide, leaving finely divided metallic lead.

The following new salts were prepared: *lithium*, $C_8H_4O_4Li_2$; *glucinum*, $C_8H_4O_4Gl.H_2O$; *manganese*, $C_8H_4O_4Mn$; *basic ferric*, $C_8H_4O_4(OH)Fe.2H_2O$; *cobalt*, $C_8H_4O_4Co.2H_2O$; *nickel*,



cerium hydrogen, $(C_8H_5O_4)_3Ce$; *mercuric*, $C_8H_4O_4Hg.H_2O$; *mercurous*, $C_8H_4O_4Hg_2.2H_2O$; *thorium*, $(C_8H_4O_4)_2Th.5H_2O$; *uranyl*,



W. G.

Diphenyltetrachlorophthalide and some of its Derivatives.

W. R. ORNDORFF and (Miss) R. R. MURRAY (*J. Amer. Chem. Soc.*, 1917, **39**, 293—304).—Tetrachlorophthalyl chloride, m. p. 118° (compare Graebe, A., 1837, 832) condenses with benzene in the presence of aluminium chloride, giving *diphenyltetrachlorophthalide*.

$C_6Cl_4 \begin{matrix} \swarrow CPh_2 \\ > O \\ \searrow CO \end{matrix}$, thick needles, m. p. 250°. This phthalide is, how-

ever, better prepared by condensing the *acetate*, white prisms, m. p. 200°, of *o*-benzoyltetrachlorobenzoic acid, with benzene in the presence of aluminium chloride. If the acetate is condensed with toluene instead of benzene, it yields *phenyltolyltetrachlorophthalide*, pale yellow needles, m. p. 201°. If tetrachlorophthalyl chloride is condensed with toluene under similar conditions, *ditolyltetrachlorophthalide*, yellow plates, m. p. 209°, is obtained. All these tetrachlorophthalides resemble one another and diphenylphthalide in their properties.

When diphenyltetrachlorophthalide is nitrated in the cold with nitric acid (D 1.52) a mixture of two *dinitro*-derivatives is obtained, of which the isomeride less soluble in benzene, having m. p. 238—240°, is formed to the lesser amount, whilst the more soluble isomeride, m. p. 162—164°, is the principal product. Traces of a

third *dinitro*-compound, m. p. 180—185°, were found. Attempts to prepare the corresponding diamino-compounds were not successful, using stannous chloride and hydrochloric acid. Reduction took place, but the product contained tin, which could not be removed.

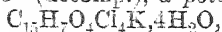
[With H. C. ALLEN.]—*o*-Benzoyltetrachlorobenzoic acid when condensed with phenol in the presence of stannous chloride yields *hydroxydiphenyltetrachlorophthalide*, colourless prisms, m. p. 268—270°, which may also be obtained by simply heating the acetate of *o*-benzoyltetrachlorobenzoic acid and phenol together at 180—190° for three hours. It gives an *acetate*, m. p. 211°.

Phenylresorcinoltetrachlorophthalein, m. p. 283—285°, was prepared by heating resorcinol and *o*-benzoyltetrachlorobenzoic acid acetate together at 160° for two hours. It crystallises from alcohol with 1EtOH and 1H₂O and from benzene with 1C₆H₆. It yields a *diacetate*, silky, white needles, m. p. 235°. W. G.

A New Class of Phthaleins (mixed Phthaleins) formed by Heating *o*-4-Hydroxybenzoylbenzoic Acid with Phenols. W. R. ORNDORFF and (Miss) R. R. MURRAY (*J. Amer. Chem. Soc.*, 1917, **39**, 679—697).—Phenolphthaleinoxime (compare Friedlander, A., 1893, i, 719) is obtained pure if less hydroxylamine hydrochloride, 12·5 instead of 15 grams, is used than recommended (*loc. cit.*). When boiled with dilute sulphuric acid, it is decomposed quantitatively, giving *o*-4-hydroxybenzoylbenzoic acid and *p*-aminophenol. The acid gives a *diacetate*, m. p. 137—140°, and when heated at 200—204° for two hours, an *anhydride*, m. p. 199—201°. When heated with various phenols, *o*-4-hydroxybenzoylbenzoic acid gave the corresponding phthalein. Thus with phenol itself a quantitative yield of phenolphthalein was obtained, no isomeric compound being formed. When heated with aniline, *o*-4-hydroxybenzoylbenzoic acid gave *phenolanilinephthaleinanilide*, colourless needles, m. p. 252—256°. It dissolves in boiling alkalis, giving a bluish-red solution of the alkali salt of the phenolanilinephthalein. Resorcinol gives two, isomeric, *phenolresorcinolphthaleins*, C₂₀H₁₄O₅, one crystallising in slender, white needles, m. p. 200—202°, the other in thicker needles or plates, m. p. 270—272°. If the crude product from this preparation is boiled with acetic anhydride for several hours, a mixture of the *mono*- and *di*-acetates is obtained, which, when boiled with sodium acetate and acetic anhydride, gives a mixture of the *tri*-acetates of the two phthaleins. These acetates are hydrolysed by boiling alcoholic alkali. *α*-Naphtholphenolphthalein could only be obtained as brown flocks, m. p. 110—130°, giving a light, yellowish-brown *diacetate*, m. p. 188—190°. *β*-Naphtholphenolphthalein was obtained as brown flocks and could not be purified, neither could its *acetate*. With *o*- and *p*-cresol, phthaleins were obtained which could not be purified.

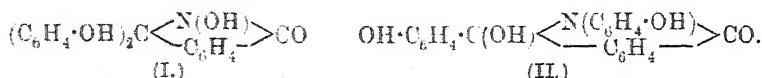
When tetrachlorophthalic anhydride is condensed with anisole in the presence of aluminium chloride, 3:4:5:6-tetrachloro-2-*p*-anisoylbenzoic acid, m. p. 182°, and some of the dimethyl ether of phenoltetrachlorophthalein (compare Orndorff and Black, A., 1909, i, 389) are formed. The acid gives a *sodium salt*, C₁₅H₇O₄Cl₄Na·5H₂O,

pearly leaflets, m. p. 275° (decomp.), a potassium salt,

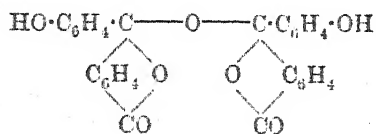


leaflets, the anhydrous salt having m. p. 245—248° (decomp.), and an acetate, $C_{17}H_{10}O_5Cl_4$, white needles, m. p. 225°. The acetate when heated with phenol at 180° for two hours yielded *phenoltetrachlorophthalein methyl ether*, white needles, m. p. 295° (decomp.).

The authors consider that the decomposition of phenolphthalein oxime is best explained by assigning to it the constitution (I), the oxime undergoing the Bechmann rearrangement to the compound (II) before decomposition. This is supported by the fact that



p-hydroxyphthalanil is obtained if excess of hydroxylamine is used in the preparation of the oxime. The hydroxyl groups in both 2-*p*-anisoylbenzoic acid and *p*-aminophenol, both being in the para-position, they must also occupy *para*-positions in phenolphthalein itself, which is therefore not a mixture of two isomerides. The easy and quantitative conversion of 2-*p*-anisoylbenzoic acid into phenolphthalein by heating the acid



alone with phenol supports the theory that this acid is an intermediate product in the formation of phenolphthalein from phthalic anhydride and phenol.

The anhydride obtained from 2-*p*-anisoylbenzoic acid is assigned the annexed constitution. It resembles the phthaleins very closely in its properties and decomposes into phenolphthalein and phthalic anhydride when heated.

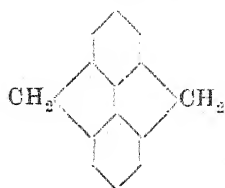
W. C.

Quinone-phenolate Theory of Indicators. Electrical Conductivity of Solutions of Phenolsulphonephthalein and of its Bromo- and Nitro-derivatives. E. C. WHITE and S. F. ACREE (*J. Amer. Chem. Soc.*, 1917, **39**, 648—652. Compare A., 1908, i, 653; 1909, i, 650).—The molecular conductivities and colours of approximately 0.001*N*-aqueous solutions of phenolsulphonephthalein, tetrabromophenolsulphonephthalein, and tetranitrophenolsulphonephthalein have been determined. The results show that these indicators are in the quinonoid form to the extent of at least 60%. The yellow colour is dependent on the quinone group and not appreciably on the primary ionisation, that of the sulphonic acid group. A comparison of the colours, conductivities, and p_H values of the first two of these substances with those of the last shows that the intense red or blue colours develop simultaneously with the secondary ionisation, that of the phenol group, and thus with the formation of quinone-phenolate ions.

J. F. S.

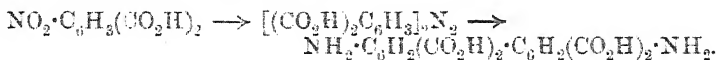
Some Products of the Reduction of 5-Nitroisophthalic Acid. RICHARD MEYER and HANS WESCHE (*Ber.*, 1917, **50**, 442—452).—In view of the possibility that a hydrocarbon of the

annexed formula might be present in coal tar or in the tar obtained during pyrogenic condensations of acetylene, the authors have tested various methods whereby it might be synthesised, but have found nothing serviceable yet.



Condensations between methylene chloride or carbonyl chloride and diphenyl or fluorene under the influence of aluminium chloride were entirely without result.

Another effort had for its aim the production of diphenyl-2:6:2':6'-tetracarboxylic acid, which ought to lose carbon dioxide on heating and give the diketone corresponding with the above formula. For this purpose, 5-nitroisophthalic acid was treated as indicated, but the difficulties became too great at the stage of the benzidine-tetracarboxylic acid:



*iso*Phthalic acid is best nitrated by boiling with pure nitric acid. The alkaline reduction of 5-nitroisophthalic acid may be effected by means of sodium amalgam or zinc dust, but best of all electrolytically. The product is *azobenzene-3:5:3':5'-tetracarboxylic acid*, which crystallises in reddish-yellow filaments, decomp. 390° , and forms a *sodium* salt, $10\text{H}_2\text{O}$, bundles of yellow needles, and a *methyl* ester, reddish-yellow prisms, m. p. $223-224^\circ$. For the reduction and transformation of this acid, it is boiled with hydrochloric acid and tin, but much aminoisophthalic acid is always formed. *Benzidine-2:6:2':6'-tetracarboxylic acid* crystallises in clusters of greenish-yellow needles, decomp. 300° .

The reduction of 5-nitroisophthalic acid to an azoxy-acid is best effected by means of alkaline sodium arsenite solution. *Azoxybenzene-3:5:3':5'-tetracarboxylic acid* crystallises in pale brown leaflets, decomp. above 360° , and the *methyl* ester in slender, pale yellow needles, m. p. $231-232^\circ$.

For the preparation of 5-aminoisophthalic acid, it is most convenient to reduce the nitro-acid with sodium hyposulphite. 5-Acetylaminoisophthalic acid crystallises in pale red needles, decomp. $314-315^\circ$, and the *benzoyl* derivative in prisms, decomp. above 360° . J. C. W.

Hemimellitic Acid. RICHARD MEYER and HANS WESCHE (*Ber.*, 1917, 50, 452-455).—A further attempt to prepare diphenyl-2:6:2':6'-tetracarboxylic acid (preceding abstract) was by the electrolysis of a solution of *sodium 1:3-dimethyl hemimellitate*, $\text{C}_6\text{H}_3(\text{CO}_2\text{Me})_2 \cdot \text{CO}_2\text{Na} \cdot 6\text{H}_2\text{O}$, which crystallises in rectangular prisms, but this method also gave no result.

In methylating hemimellitic acid, the experience was gained that the fact that one of the carboxyl groups is surrounded by the others does not prevent its esterification, but only postpones it. J. C. W.

The Tinctorial Constituents of some Lichens which are used as Dyes in Ireland. HUGH RYAN and W. M. O'RIORDAN (*Proc. Roy. Irish Acad.*, 1917, **33**, 91—104).—A chemical examination has been made of four typical lichens which are used domestically for dyeing wool yellowish-brown shades, and a decision arrived at in each case as to the constituent to which the tinctorial properties are mainly due.

Parmelia saxatilis, Ach., yielded stereocaulic acid (soluble in ether) and salazinic acid (extracted by acetone), and although the latter is a colourless substance, it is the chief dyeing constituent, the dye proper being most probably an oxidation product.

Ramalina scopulorum, Ach., gave *d*-usnic and scopuloric acids, the tinctorial properties being due to the latter. It is suggested that salazinic and scopuloric acids are homologues of the formula $C_{17}H_{14}O_9$ and $C_{18}H_{16}O_9$ respectively.

Ramalina cuspidata, Nyl., yielded *d*-usnic acid, and the acid to which the dyeing properties are due was apparently cuspidatic acid, which might have the formula $C_{17}H_{16}O_{10}$.

Physcia parietina, De Not., is not used much for dyeing, and its chief constituent, physcione (frangula-emodin monomethyl ether), is practically devoid of tinctorial properties, which might scarcely be expected of a derivative of trihydroxyanthraquinone, if, as according to Fischer and Gross (A., 1911, i, 886), it is such a compound.

The chemical examination of these lichen acids agrees in the main with the classical work of Zopf and Hesse. J. C. W.

The *m*-Homosalicylaldehydes and their Derivatives. O. ANSELMINO (*Ber.*, 1917, **50**, 395).—The two aldehydes are obtained from *m*-cresol by the Tiemann-Reimer reaction and separated by conversion into their anils. 4-Methylsalicylaldehyde has m. p. 60—61°, and forms a solid anil, m. p. 93°, whilst 6-methylsalicylaldehyde has m. p. 32° and gives a liquid anil. The phenylhydrazones have m. p. 161° and 172°, and the semicarbazones 268° and 212—214° (decomp.) respectively (compare Chuit and Bolsing (A., 1906, i, 282). J. C. W.

A New Method for preparing Cyclic Ketones. FRITZ ULLMANN (*Ber.*, 1917, **50**, 403—405. Compare A. Schaarschmidt, this vol., i, 285).—Polemical. Questions of priority and patent specifications. J. C. W.

A New Synthesis of Aromatic Ketones. II. Artificial Production of Maclurin and Related Ketones. KURT HOESCH and THADÄUS VON ZARZECKI (*Ber.*, 1917, **50**, 462—468; 660. Compare A., 1915, i, 820).—An extension of Hoesch's process to more complicated phenolic ketones, culminating in the synthesis of maclurin.

Vanillonitrile (Marcus, A., 1892, 318) and phloroglucinol are dissolved in ether, mixed with anhydrous zinc chloride, and submitted

to a current of hydrogen chloride, when the ketone-imide hydrochloride separates as a crystalline mass. On boiling with water, this salt is hydrolysed to *vanillophloroglucinol* [2:4:6:4'-*tetrahydroxy-3'-methoxybenzophenone*], which crystallises in yellow needles, with $1\text{H}_2\text{O}$, decomp. above 200° . *Vanillogresorcinol* [2:4:4'-*trihydroxy-3'-methoxybenzophenone*] forms bundles of pale yellow needles, m. p. 210° .

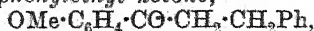
Protocatechualdoxime, brilliant yellow needles, m. p. 157° (Wegscheider gave $149\text{--}151^\circ$, A., 1896, i, 612) is converted into *protocatechuonitrile diacetate* (3:4-*diacetoxybenzonitrile*), needles, m. p. 87° , by boiling with acetic anhydride, and this is hydrolysed to protocatechuonitrile, pale yellow needles, m. p. 156° (compare Ewins, T., 1905, 95, 1488). This condenses with phloroglucinol in the above manner, forming maclurin (2:4:6:3':5'-*pentahydroxybenzophenone*), the synthetic product being identical in properties with the natural substance.

J. C. W.

Anisoylphenylethylene Oxide and other Keto-oxido-compounds. HENRIK JÖRLANDER (*Ber.*, 1917, 50, 406—420. Compare this vol., i, 221—225).—The behaviour of anisoylphenylethylene oxide towards alkali hydroxides and acetic anhydride is described.

When boiled for a few moments with dilute alcoholic sodium hydroxide, the oxide suffers rearrangement into *anisyl o-hydroxystyryl ketone*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}(\text{OH})\cdot\text{CHPh}$, which crystallises in odourless leaflets, m. p. 98° , and gives a dark brownish-violet colour with ferric chloride. This compound is the enolic form of *anisylbenzylglyoxal* [*anisyl benzyl diketone*], $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, into which it passes to a certain extent on keeping. This *aa*-diketone is conveniently obtained from the mono-oxime (below) by hydrolysis with hydrochloric acid. It is a yellow oil with an odour like that of benzaldehyde. It only reacts with ferric chloride after a time, and may be transformed into the enol by careful treatment with sodium ethoxide. Typical derivatives of the enol or diketone were obtained as follows: *benzoate*, leaflets, m. p. 117° ; 3-*anisyl-2-benzylquinoxaline*, needles, m. p. 137° ; *anisyl benzyl diketone phenyl-osazone*, yellow prisms, m. p. 156° ; *anisyl a-bromomenzyl diketone*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}\cdot\text{CHBrPh}$, pale yellow leaflets, m. p. 68° ; *anisyl benzyl diketoxime*, leaflets, m. p. 194° (decomp.), by mixing the compound with hydroxylamine and sodium hydroxide in excess; *anisylbenzylketoxime*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CH}_2\text{Ph}$, colourless needles, m. p. 109° , by boiling the compound with alcoholic hydroxylamine hydrochloride.

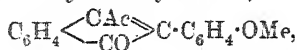
The constitution of this mono-oxime is proved by the fact that it can be obtained (in very small yield) by the action of amyl nitrite on *anisyl β -phenylethyl ketone*,



colourless leaflets, m. p. 97° . This ketone is readily obtained by the reduction of anisoylphenylethylene oxide with zinc and acetic acid or less economically from benzylidene-*p*-methoxyacetophenone. In the latter reduction, $\gamma\delta$ -*diphenyl- $\alpha\zeta$ -dianisylhexane- $\alpha\zeta$ -dione* is

also formed as a mass insoluble in alcohol, but crystallising from nitrobenzene in colourless needles, m. p. 251°.

If the original oxide is boiled with sodium hydroxide for a longer period, the diketone first formed suffers the benzil transformation into *α-hydroxy-β-phenyl-α-anisylpropionic acid*, prisms, m. p. 182° (decomp.), and a smaller quantity of another acid which is more soluble in alcohol and may be *α-hydroxy-β-phenyl-β-anisylpropionic acid*, prisms, m. p. 182° (m. p. of mixture, about 160°). When the former of these acids is boiled with acetic anhydride and sodium acetate, it loses the elements of water and forms *β-phenyl-α-anisyl-acrylic acid*, needles, m. p. 132—133°. This gives a dark red solution in sulphuric acid, and on diluting and adding alkali hydroxide the colour changes to dark bluish-violet. If boiled for a few moments with acetic anhydride and sulphuric acid, however, the above hydroxy-acid yields *3-acetyl-2-anisylindone*,



pale red, microscopic needles, m. p. 241°, whilst glacial acetic acid and sulphuric acid convert it into *2-anisylindone*, a dark red powder, m. p. 263—265°.

Anisoylphenylethylene oxide does not react with acetic anhydride alone, even on boiling, but if the agent is mixed with sulphuric acid, a certain amount of *anisoylphenylethylene glycol diacetate*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}(\text{OAc}) \cdot \text{CHPh} \cdot \text{OAc}$, needles, m. p. 160°, is formed in the cold. This suffers rearrangement as well as hydrolysis when treated with sodium hydroxide or dilute sulphuric acid, the product being anisyl benzyl ketone, which crystallises in leaflets, m. p. 77° (Meisenheimer and Jochelson, A., 1907, i, 861), and may also be obtained by the oxidation of the above hydroxy-acid with potassium dichromate and acetic acid.

The above reaction whereby enolic forms of *α*-diketones can be prepared readily from ethylene oxides has been extended to other cases. Thus, benzoylphenylethylene oxide undergoes rearrangement into *phenyl ω-hydroxystyryl ketone*, $\text{OH} \cdot \text{CBz} : \text{CHPh}$, which crystallises in many-sided forms, m. p. 85—86°, and yields a *benzoate*, rhombic leaflets, m. p. 108—109°, and *2-phenyl-3-benzylquinoxaline* (Widman, A., 1916, i, 407). The compound separates at first as a yellow oil, which contains the ketonic form, phenyl benzyl diketone. As in the above case, this *α*-diketone may be obtained by hydrolysing the mono-oxime, benzoyl benzyl ketoxime (*isonitrosobenzylacetophenone*), $\text{CH}_2\text{Ph} \cdot \text{CBz} : \text{N} \cdot \text{OH}$ (Wieland, A., 1903, i, 836), which may be prepared from the enol. *Phenylbenzyl-diketonephenylosazone*, m. p. 131°, *phenyl benzyl diketoxime*, m. p. 207°, and *phenyl α-bromobenzyl diketone*, m. p. 63°, are other typical derivatives obtained from the enol.

Benzoylphenylethylene oxide may also be converted, as in the above case of the anisoyl derivative, into *benzoylphenylethylene glycol diacetate*, $\text{OAc} \cdot \text{CHBz} \cdot \text{CHPh} \cdot \text{OAc}$, which crystallises in prisms, m. p. 107°, and may be transformed into deoxybenzoin by warming with alcoholic alkali hydroxide.

ω-Chloro-*o*-methoxyacetophenone (Tutin, T., 1910, 97, 2503)

reacts with benzaldehyde to form *o*-methoxybenzoylphenylethylene oxide, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH} \begin{smallmatrix} \text{CHPh} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$, which crystallises in colourless prisms, m. p. 124° , and may be transformed into *o*-methoxyphenyl ω -hydroxystyryl ketone, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}(\text{OH}) \cdot \text{CHPh}$, leaflets, m. p. 118° . 3-*o*-Methoxyphenyl-2-benzylquinoxaline is obtained from this in short prisms, m. p. 101.5° .

p-Toluoylphenylethylene oxide, leaflets, m. p. 85° , yields *p*-tolyl ω -hydroxystyryl ketone, prisms, m. p. $89-90^\circ$, and this, 3-*p*-tolyl-2-benzylquinoxaline, slender needles, m. p. $112-113^\circ$. It also forms *p*-toluoylphenylethylene diacetate, short prisms, m. p. 100° .

p-Chlorobenzoylphenylethylene oxide, needles, m. p. 123° , yields *p*-chlorobenzoylphenylethylene diacetate, short prisms, m. p. 110° , and also *p*-chlorophenyl ω -hydroxystyryl ketone, prisms, m. p. 103° , and this gives rise to 3-*p*-chlorophenyl-2-benzylquinoxaline, needles, m. p. 133° .
J. C. W.

Unsaturated Ketones Derived from Diacetylresorcinol. JOSEPH ALGAR (*Proc. Roy. Irish Acad.*, 1917, **33**, 109-116).—Derivatives of diflavone and diflavanone having been obtained from benzylidene compounds of diacetylresorcinol (Ryan and O'Neill, A., 1915, i, 707, 1071), diacetylresorcinol has been investigated for the same purpose. Several benzylidene derivatives are now described, but attempts to condense them to the desired compounds were not successful.

The product of the action of aluminium chloride at 160° on orcinol diacetate is identical with the diacetylresorcinol described by Collie (T., 1904, **85**, 978). It forms a *dimethyl ether* (2:4-diacetyl-3:5-dimethoxytoluene), which is a colourless oil, b. p. $195-197^\circ/30$ mm., and it reacts with aldehydes in alcoholic-alkaline media to give benzylidene derivatives (distyryl diketones). The *dibenzylidene* compound, $\text{C}_6\text{HMe}(\text{OH})_2(\text{CO} \cdot \text{CH} \cdot \text{CHPh})_2$, is a pale yellow solid, m. p. $143-153^\circ$; the *dianisylidene* compound crystallises in orange prisms, m. p. $231-232^\circ$; the *diveratrylidene* compound forms orange-yellow prisms, m. p. $188-189.5^\circ$; the *dipiperonylidene* compound exists in one modification, " α ," as orange-yellow prisms, m. p. $236-237^\circ$, and in a sparingly soluble form, " β ," yellow prisms, m. p. $248-249^\circ$, which may possibly be a flavanone, for it seems to be produced from the α -form by the action of hot hydrochloric acid.
J. C. W.

Reduction in Concentrated Sulphuric Acid Solution by Means of Aluminium Powder. ALFRED ECKERT and RUDOLF POLLAK (*Monatsh.*, 1917, **38**, 11-17).—The authors have studied the reaction described in D.R.-P. 190656 and 201542, by which anthraquinone derivatives are reduced in concentrated sulphuric acid solution by either copper or aluminium powder. In order to carry out the reduction, they dissolve the substance in 20-30 times its weight of concentrated sulphuric acid, and to the well-cooled mixture one-fifth of the weight of substance of aluminium powder

is slowly added with continuous shaking and cooling. The end of the reaction is indicated by foaming. When the reduction is complete, the mixture is poured into cold water and the product extracted with a suitable solvent. In this way, anthraquinone has been reduced to anthraquinol and anthrone; benzophenone into β -benzpinacolin; benzoylbenzoic acid into the dilactone of dihydroxytetraphenylethanedicarboxylic acid. If the reduction is effected with the further addition of acetic acid or benzoic acid or their anhydrides, the products are either the diacetylated or dibenzoylated derivatives of the reduced original substance. Thus, 5 grams of anthraquinone reduced by 1 gram of aluminium powder in 100 grams of concentrated sulphuric acid and 30 grams of glacial acetic acid yields the diacetyl derivative of anthraquinol. The dibenzoyl derivative is obtained in a similar manner. Acridone cannot be reduced by the above method. *p*-Chlorobenzoylbenzoic acid when reduced by aluminium powder yields the corresponding dilactone. When the dilactone of dihydroxytetraphenylethanedicarboxylic acid is heated with 20% fuming sulphuric acid for three hours at 180°, it is converted into sulpho- β -anthraquinonecarboxylic acid.

J. F. S.

A Hydrate of Sodium Anthraquinone-2:7-disulphonate.

M. L. CROSSLEY (*J. Amer. Chem. Soc.*, 1917, **39**, 122—124).—The salmon-pink compound isolated in the separation of anthraquinone-2:6- and -2:7-disulphonic acids (compare A., 1915, i, 975) is shown to be a *hydrate* of sodium anthraquinone-2:7-disulphonate, the addition of the elements of water taking place, probably, through one of the carbonyl oxygens, this best accounting for all the properties of the substance.

W. G.

The Caoutchouc from *Eucommia ulmoides*, Oliver. ARTHUR F. SIEVERS (*J. Amer. Chem. Soc.*, 1917, **39**, 725—731. Compare Weiss, *Trans. Linn. Soc.*, 1888—1894, [ii], **3**, 243).—An examination of the elastic constituent of *Eucommia ulmoides* with reference to its behaviour towards solvents. Qualitative and quantitative tests were made of its solubility in ether, light petroleum, toluene, chloroform, carbon disulphide, and carbon tetrachloride, and in this respect it was compared with samples of caoutchouc from Siam and Ceylon. The material from *Eucommia* does not swell up with the solvents, but becomes very soft and spreads over the bottom and sides of the containing vessel.

W. G.

An Iodine Additive Product of Coumarin. ARTHUR W. DOX and W. G. GAESSLER (*J. Amer. Chem. Soc.*, 1917, **39**, 114—117).—When an aqueous solution of potassium iodide (1 mol.) is added to an alcoholic solution of coumarin (2 mols.) and iodine (2 mols.), black, needle-shaped, lustrous crystals are formed, which seem to be an iodide of coumarin. When washed with

water, the compound decomposes into coumarin and iodine, and if treated with a solvent which does not dissolve potassium iodide, the only products obtained from the solution are coumarin and iodine. The compound contains from 30·5—31·7% of iodine, according to analyses, and a small, variable amount of potassium iodide, which probably is there as an impurity from the mother liquor. Substitution of the iodine in the coumarin molecule has not taken place, and the compound probably has the composition $(C_9H_6O_2)_4I_2$. W. G.

The Nitration Products of Tetrachlorofluoran and some of their Derivatives. W. R. ORNDORFF and J. J. KENNEDY (*J. Amer. Chem. Soc.*, 1917, **39**, 88—103).—By nitrating tetrachlorofluoran under different conditions, five nitro-derivatives have been prepared, and subsequently reduced to the corresponding amino-compounds.

Tetrachlorofluoran is now found to have m. p. 290—291° (decomp.) (compare Orndorff and Black, A., 1909, i, 389). When nitrated in acetic acid solution with nitric acid (D 1·5), the mixture being heated to boiling, tetrachlorofluoran yields *tetrachloro-2-nitrofluoran*, m. p. 317—318°, which is practically insoluble in most of the ordinary organic solvents. It crystallises from glacial acetic acid. It dissolves unchanged in cold concentrated sulphuric acid. When reduced in an alcoholic solution of stannous chloride saturated with hydrogen chloride, it yields *tetrachloro-2-amino-fluoran*, m. p. 279—280°, which when diazotised and boiled with water gives tetrachlorofluoran instead of the expected hydroxyl derivative. If an excess of nitric acid is used in the above nitration, the product is a mixture of *tetrachloro-2:7-dinitrofluoran*, m. p. 317—318°, and *tetrachloroisodinitrofluoran*, m. p. 249—250°, in which the nitro-groups are probably in the positions 2 and 5. These two isomerides are best separated by crystallisation from methyl alcohol, the first-named being the less soluble of the two. The 2:7-dinitro-compound when reduced as described above yields *tetrachloro-2:7-diaminofluoran*, orange needles, m. p. above 325°. The colour reactions correspond with those of diaminofluoran (compare Meyer and Friedland, A., 1898, i, 590). It gives a colourless *hydrochloride*. When diazotised in sulphuric acid solution and boiled with water, it yields *quinoltetrachlorophthalein*, faint yellow crystals, m. p. above 325°.

When tetrachlorofluoran is dissolved in nitric acid (D 1·5) and the solution heated on a water-bath, it yields *tetrachloro-2:5:7-trinitrofluoran*, yellow crystals, m. p. 275—276°; this on reduction gives *tetrachloro-2:5:7-triaminofluoran*, m. p. above 325°, which when diazotised and boiled with water gives a *phthalein*, which was not characterised.

Tetrachlorotetranitrofluoran, m. p. above 325°, was obtained by nitrating the trinitro-compound in a mixture of nitric acid (D 1·5) and sulphuric acid (D 1·84), or by nitrating the original tetrachlorofluoran in a similar mixture. On reduction it yielded *tetra-*

chlorotetra-aminofluoran, m. p. above 325°. No pentanitro-derivative could be obtained.

The nitro- and two isomeric dinitro-compounds are not affected by aqueous alkali hydroxides, but dissolve in hot alcoholic potassium hydroxide with a yellow colour. The tri- and tetra-nitro-compounds are slightly soluble in hot aqueous alkali hydroxides and readily so in cold alcoholic potassium hydroxide with an orange colour. In each case an ortho-quinonoid salt is probably formed. The salts of the tri- and tetra-nitro-compounds are quite stable, but the others are decomposed on the addition of water.

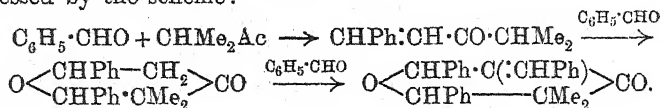
The amino- and diamino-tetrachlorofluorans dissolve in hot alcoholic potassium hydroxide with a yellow colour and the tri- and tetra-amino-compounds with a reddish-orange colour. The ortho-quinonoid salts probably formed are stable, no precipitation occurring on the addition of water.

The solubility of tetrachlorofluoran in concentrated sulphuric acid decreases with the successive introduction of nitro-groups into the molecule.

W. G.

Condensation of Aldehydes with Ketones. III. Benzaldehyde with Methyl *iso*Propyl Ketone. HUGH RYAN and PHYLLIS RYAN (*Proc. Roy. Irish Acad.*, 1917, **33**, 105—108. Compare A., 1915, i, 416; 1916, i, 654).—In their explanation of the formation of a tetrahydropyrone, $C_{25}H_{22}O_2$, from benzaldehyde and dimethylacetylacetone or "monomethylacetylacetone," Ryan and Dunlea assumed that styryl ethyl ketone was an intermediate product. Later it was shown that this ketone did not give the same tetrahydropyrone when condensed with benzaldehyde, which rendered a revision of the explanation necessary.

It is now found that the compound in question is produced by the condensation of benzaldehyde with methyl *isopropyl* ketone, that is, with a hydrolytic product of dimethylacetylacetone, and not of monomethylacetylacetone. The wrong conclusion was mainly due to the fact that the monomethylacetylacetone used previously contained some of the dimethyl compound. The formula of the compound must therefore be altered to that of 2:6-diphenyl-3-benzylidene-5:5-dimethyltetrahydropyrone, and its formation be expressed by the scheme:



Pure methylacetylacetone condenses with benzaldehyde in alcoholic hydrogen chloride to form Ryan and Devine's compound, $C_{25}H_{20}O$, whilst ethyl α -acetylbutyrate gives α -benzylideneacetylbutyric acid, $CHPh \cdot CH \cdot CO \cdot CHEt \cdot CO_2H$, m. p. 152° (decomp.).

J. C. W.

Preparation of Cephaeline *iso*Amyl Ether and Salts Thereof. J. W. MEADER (*Brit. Pat.*, 103881, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 402—403. Compare this vol., i, 91).—*Cephaeline*

isoamyl ether, probably $C_{28}H_{37}O_3N_{20} \cdot C_5H_{11}$, is produced by treating cephaeline with an alkali metal and an *isoamyl* haloid. It is a varnish-like substance, easily soluble in alcohol, ether, or chloroform. It dissolves in acids to form salts, the *hydrobromide* crystallising in colourless needles. The ether and its salts are valuable medicinal products. H. W.

Chelerythrine. P. KARRER (*Ber.*, 1917, 50, 212—221).—The most interesting facts known about the alkaloid chelerythrine (in plants of the order *Papaveraceae*) hitherto are that it is a colourless base which forms highly coloured salts and that it holds combined alcohol ($C_{21}H_{17}O_4N \cdot EtOH$) and water ($\frac{1}{2}H_2O$) very firmly attached (compare Schmidt and co-workers, A., 1901, i, 742—744). It is now found to be a reactive substance. It contains a carbonyl group, and the remarkable discovery is made that any derivatives in which this group is altered, although they still contain nitrogen, are no longer basic. Chelerythrine, therefore, is the first alkaloid of which it can be said that it owes its basic properties to some atom other than nitrogen. It may be that an oxygen atom performs this function, the salts being oxonium salts.

Chelerythrine, recrystallised once from 96% alcohol, then four times from ethyl acetate, corresponds with the formula $C_{21}H_{17}O_4N \cdot EtOH$, and has m. p. 199°. The hydrochloride, $B \cdot HCl \cdot \frac{1}{2}H_2O$, crystallises well, and loses its water only after some days in an evacuated desiccator. From the salt, preparations free from alcohol, such as $B \cdot \frac{1}{2}H_2O$, m. p. 250°, can be prepared by precipitation.

If to the orange-coloured solution of the hydrochloride is added a potassium cyanide solution, a compound, $(C_{21}H_{15}O_4N) \cdot CN$, is at once precipitated, which crystallises in colourless tablets or leaflets, m. p. 221° (another preparation gave 248°). This substance is indifferent to the action of dilute hydrochloric acid or sodium hydroxide, but the cyanogen residue is removed by boiling with alcoholic silver nitrate or concentrated hydrochloric acid.

The *phenylhydrazone*, $(C_{21}H_{19}O_4N) \cdot N \cdot NHPh$, m. p. 158°, is white, but gradually becomes brown even in a high vacuum. The compound with acetylacetone, $(C_{21}H_{19}O_4N) \cdot CAC_2$, forms long, snowy needles, and the compound with *p*-nitrobenzyl cyanide, $(C_{21}H_{19}O_4N) \cdot C(CN) \cdot C_6H_4 \cdot NO_2$, is pale yellow.

Grignard agents react with chelerythrine to give non-basic alkyl derivatives of a residue, $C_{16}H_{12}O_3N$, which is designated "*chelalbin*." *Methylchelalbin*, $C_{16}H_{12}O_3NMe$, *ethylchelalbin*, and *propylchelalbin* crystallise readily, but the m. p.'s depend on the m. p. of the original base.

Chelerythrine can also be reduced to the pure white, non-basic *dihydrochelerythrin*, m. p. 143—144°, by means of zinc or tin and hydrochloric acid. J. C. W.

The Alkaloids of the Pomegranate Tree. I. Pelletierine. KURT HESS (*Ber.*, 1917, 50, 368—379).—Of the five alkaloids which are recognised as constituents of the rind of the root of the

pomegranate tree (compare Tanret, A., 1878, 739; Ciamician and Silber, A., 1894, i, 154; and Piccinini, A., 1900, i, 110), only the crystalline ψ -pelletierine has been investigated at all closely and proved to be a homologue of tropinone. The main constituent, pelletierine, is an oil which is very sensitive towards atmospheric oxygen, and beyond the fact that it has the formula $C_8H_{15}ON$, little else is known about it. It is now demonstrated that it is a secondary base and that it contains a carbonyl group adjacent to a reactive methylene group. It cannot be a bicyclic base, but it may possibly contain a piperidine ring, although no evidence can be given as yet. These new facts are therefore summed up in the formula $C_6H_{12}(NH)(\cdot CO \cdot CH_2 \cdot)$.

Pelletierine hydrochloride has m. p. 143—144°, and is not hygroscopic when pure, as Tanret stated; the *hydrobromide* crystallises extremely well in fan-like aggregates, m. p. 140°; the *picrate* has m. p. 150—151°. The *N-acetyl* compound, b. p. 173—174°/18 mm., and *N-benzoyl* derivative, prisms and plates, m. p. 75°, are formed by the action of the acyl chloride in the presence of sodium hydroxide. They are practically neutral, are stable, and yield *aureichlorides*, m. p. 95—96° and 139° (decomp.) respectively.

Pelletierine can be methylated by heating with formaldehyde and formic acid in a sealed tube at 135—143°. The *methylpelletierine* obtained in this way is an oil, b. p. 98—102°/14 mm., with a powerful narcotic odour, and is even more sensitive to air than pelletierine. The *hydrobromide*, $C_9H_{17}ON \cdot HBr$, forms long, stable, prismatic needles, m. p. 152°, and the *semicarbazone hydrochloride*, prismatic rods, m. p. 168—169° (decomp.). Apparently, this base is not identical with Tanret's methylpelletierine or Piccinini's *isomethylpelletierine*, but these natural bases must be examined before a definite opinion can be expressed.

Pelletierine hydrobromide reacts with semicarbazide hydrochloride to give a double compound of the semicarbazone hydrobromide and semicarbazone hydrochloride, $C_{18}H_{38}O_2N_8ClBr \cdot \frac{1}{2}H_2O$, m. p. 188° (decomp.). The simple *semicarbazone hydrochloride*, $C_9H_{19}ON_4Cl$, is obtained from the free alkaloid, in radiating groups of prisms, decomp. 188°.

The presence of one reactive methylene group, and the possibility of enolisation taking place, are shown by the formation of the following derivatives: *isonitrosobenzoylpelletierine*, $C_{17}H_{18}O_3N_2$, long, thin tablets, m. p. 192—193°, by the action of amyl nitrite; *benzylidenepelletierine hydrochloride*, $C_{17}H_{20}ONCl$, m. p. 187°, and *benzylidenepelletierine chlorobromide*, $C_{30}H_{40}O_2N_2ClBr \cdot H_2O$, m. p. 198°, by the action of benzaldehyde; *diacetylpelletierine*, $C_{12}H_{19}O_3N$, a very viscous, yellow oil, b. p. 145—155°/14 mm., which loses acetic acid when kept, but is stable towards oxygen and is formed by boiling pelletierine hydrobromide with acetic anhydride.

J. C. W.

Alkaloids of the Pomegranate Tree. II. Tanret's Methylpelletierine and Piccinini's isoMethylpelletierine. K. Hess and A. EICHEL (*Ber.*, 1917, 50, 380—384).—In order to investigate

these companion alkaloids of pelletierine, some root bark of the pomegranate has been treated according to Tanret and Piccinini's directions, when 40 grams of pure pelletierine hydrobromide and 21.5 grams of an oil containing the other bases were isolated from 100 kilos. of material. The oil has now been separated by fractionation under reduced pressure in an atmosphere of hydrogen into ψ -pelletierine, b. p. 140°/20 mm., m. p. 53—54° (Tanret gave m. p. 48°), and Piccinini's *isomethylpelletierine*, b. p. 100—115°/20 mm., picrate, m. p. 158°, semicarbazone hydrochloride, m. p. 208—209° (decomp.) (compare A., 1900, i, 110). No trace of Tanret's optically active methylpelletierine could be found in this specimen. Perhaps Piccinini's compound is the racemide of Tanret's base, or more probably the latter was impure. The base is certainly not identical with, although so similar to, α -1-methylpiperidyl-2-propanone (A., 1916, i, 67). A very small quantity of a stable methylpelletierine quite identical with this ketone was found, however, in the first runnings, b. p. 101—103°/19 mm., of the above distillation. J. C. W.

Action of Aldehydes on Hydramines of the Pyrrolidine and Piperidine Series. IV. A Method for Alkylating Secondary Amino-alcohols. K. HESS, Ch. UIBRIG, and A. EICHEL (*Ber.*, 1917, 50, 344—351).—The alkylation of secondary amino-alcohols has always been difficult of achievement, even by the use of formaldehyde, because the hydroxyl group usually suffers oxidation in this process (A., 1916, i, 67). It has already been shown in one case, however (*ibid.*), that if formic acid is present, this substance undergoes oxidation more readily than the amino-alcohol, and so a *N*-methylated hydramine can be obtained. This is found to be a general reaction, and other examples are now given.

α -2-Pyrrolidylbutyl alcohol (*ibid.*) is heated with formic acid and 40% formaldehyde solution at 105—110° in a sealed tube, and so converted into α -1-methyl-2-pyrrolidylbutyl alcohol, a colourless oil with a faint, basic odour, b. p. 89—92°/16 mm., which forms a *picrate*, stout crystals, m. p. 113—114°, and an *acetate*, $\text{CH}_2\text{-OH}$
 $\text{CH}_2\text{-NMe} \rangle \text{CH}\cdot\text{CHPr}\cdot\text{OAc}$, a limpid, mobile oil, b. p. 94—97°/13 mm., and resists the hydrolytic action of boiling hydrochloric acid.

β -6-Picolyl-2-ethyl alcohol is converted in like manner into β -1:6-dimethylpyridyl-2-ethyl alcohol, b. p. 114—118°/18 mm., which forms an *acetate*, b. p. 114—119°/16 mm.

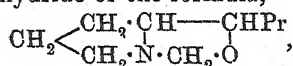
The production of α -2-pyridylpropan- β -ol by the condensation of acetaldehyde with picoline is not economical. A yield of 54 grams from 940 grams of technical picoline is reported. This base, however, can be reduced quantitatively by means of catalysed hydrogen, and the specimen of α -2-piperidylpropan- β -ol obtained on this occasion had b. p. 114—115°/16 mm., crystallised in rectangular tablets, m. p. 69—70°, and yielded a *hydrochloride*, m. p. 133°. The methylation of this hydramine by the above process also proceeds smoothly. α -1-Methylpiperidyl-2-propan- β -ol (Ladenburg, A., 1898,

i, 688) is a pleasant-smelling base, b. p. 104—107°/10 mm., which forms a *picrate*, bundles of small rods, m. p. 178°, an *acetate*, b. p. 109—112°/17 mm., and a limpid, viscous *benzoate*, b. p. 176—178°/16 mm.

Scopoligenine can also be converted into very pure scopoline by methylation in this way.

J. C. W.

Action of Aldehydes on Hydramines of the Pyrrolidine and Piperidine Series. V. Scission of Tertiary Methyl-amino-ketones into Formaldehyde and Secondary Hydramine Bases. K. HESS, A. EICHEL, and CL. UIBRIG (*Ber.*, 1917, 50, 351—365. Compare A., 1916, i, 67).—In the case of some of the *tert.*-methylamino-ketones which were prepared by the action of formaldehyde on secondary hydramines, no direct proof of the presence in them of a carbonyl group could be obtained, for the usual reagents, hydroxylamine, semicarbazide, and phenylhydrazine, brought about the hydrolysis of the amino-ketone to the original hydramine and formaldehyde. It might conceivably be that in the case of 1-methyl-2-pyrrolidyl propyl ketone, for example, the compound is really an anhydride of the formula,



and so, in order to decide definitely whether genuine *tert.*-methyl-amino-ketones can be hydrolysed in this way, α -1-methylpiperidyl-2-propan- β -one has been prepared by the oxidation of the corresponding isopropyl alcohol (preceding abstract) and tested in its behaviour towards semicarbazide. It is found that under one set of conditions the ketone yields a semicarbazone, whilst under others it is hydrolysed to α -2-piperidylpropan- β -ol and formaldehyde semicarbazone.

α -1-Methylpiperidyl-2-propan- β -ol is oxidised by means of chromic acid and acetic acid at 65—70°. α -1-Methylpiperidyl-2-propan- β -one is a stable, limpid oil, b. p. 107—112°/18 mm., with a pleasant, geranium-like odour. It dissolves in cold water in all proportions, but is precipitated almost completely on warming, and it reduces ammoniacal silver solutions, giving silver mirrors. The base acts locally as a powerful irritant. The *picrate* has m. p. 136—137°, and the *semicarbazone*, obtained by leaving the base with semicarbazide hydrochloride and potassium acetate in aqueous solution, crystallises in rhombohedra, m. p. 142—143°, and forms a *hydrochloride*, $\text{C}_{10}\text{H}_{20}\text{ON}_2 \cdot \text{HCl} \cdot \frac{1}{2} \text{EtOH}$, m. p. 183° (decomp.). When the base is left with semicarbazide acetate in alcoholic solution, however, *formaldehyde semicarbazone*, $\text{CH}_2 \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, crystallises out gradually in stout prisms, m. p. 169° (decomp.), and α -2-piperidylpropan- β -ol (preceding abstract) may be recovered from the mother liquor.

The authors share the experience of Thiele and Bailey (A., 1899, i, 109) in being unable to obtain a normal semicarbazone by the direct application of formaldehyde.

It was desired to effect the above hydrolysis with a specimen of 1-methyl-2-pyrrolidyl propyl ketone (A., 1916, i, 68), which should

be obtained by the oxidation of α -1-methyl-2-pyrrolidylbutyl alcohol (preceding abstract). It was found, however, that during the oxidation of this secondary alcohol the methyl group is also eliminated, the product being an imino-ketone which resembles pelletierine in properties.

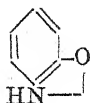
The Hofmann degradation has also been applied to 1-methyl-2-pyrrolidyl propyl ketone. When this ketone is treated with methyl iodide, it forms two quaternary *methiodides*; one is crystalline, m. p. 95° , and after treatment with silver chloride gives an *aurichloride*, $C_{10}H_{20}ONCl_4Au$; sulphur-yellow tablets, m. p. 93° , whilst the other is a syrup which similarly yields an isomeric, golden-brown *aurichloride*, m. p. 82° . When the corresponding ammonium hydroxides are distilled, they lose formaldehyde and yield the same base, $CH_3:CH:CH_2:CH(NHMe)\cdot CHPr\cdot OH$ or $NHMe\cdot CH_2\cdot CH_2\cdot CH:CH\cdot CHPr\cdot OH$, b. p. $89-91^\circ/10$ mm.

2-Pyrrolidyl propyl ketone, $\begin{array}{c} CH_2\cdot CH_2 \\ | \\ CH_2-NH \end{array} > CH\cdot COPr$, obtained by the oxidation of α -1-methyl-2-pyrrolidylbutyl alcohol by means of chromic acid, is a very strongly basic oil, b. p. $84-86^\circ/17$ mm., which very soon changes to a dark resin on exposure to the air. The *picrate* has m. p. $104-105^\circ$, the *picrotonate*, m. p. $128-129^\circ$, and the *semicarbazone* crystallises in rosettes of prismatic needles, m. p. 186° (decomp.). Although the authors do not doubt that the base is an imino-ketone, they have not been able to benzoylate it, and find that the methylation by means of formaldehyde and formic acid follows an abnormal course. The alkaline liquid left after extracting the base with ether was evaporated to dryness, when butyric acid was recognised in the vapour and hygric acid in the residue.

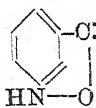
J. C. W.

Chemical Nature of the "Vitamines." III. Structure of the Curative Modifications of the Hydroxypyridines.

ROBERT R. WILLIAMS (*J. Biol. Chem.*, 1917, 29, 495-520. Compare A., 1916, i, 697, 770, 862).—The author amplifies his previous directions for the preparation of the needle-crystal form of 2-hydroxypyridine. The corresponding crystal form of 3-hydroxypyridine, and the anhydrous forms of methylpyridone, trigonelline, and betaine also produce curative effects on polyneuritic birds. It follows that the curative form of 2-hydroxypyridine is a ψ -betaine which can be represented by the annexed formula.



On decomposing nicotinic acid hydriodide with silver oxide, the filtrate from the silver haloid, on being promptly injected into a polyneuritic bird, is found to possess marked curative properties. It is suggested that the nicotinic acid thus produced has a betaine structure (annexed formula), and that the curative properties of the vitamin fractions of yeast and rice polishings are due in part to the presence of this isomeric form of nicotinic acid or a polymeride or simple derivative of it.



H. W. B.

p*

Methylation of Cyclic Amino-acids. II. Synthesis of 1-Methylhexahydronicotinic and 1-Methylhexahydro-nicotinic Acids. K. HESS and F. LEIBBRANDT (*Ber.*, 1917, 50, 385—389. Compare A., 1916, i, 75).—For the purposes of comparison with certain degradation products of pelletierine, the authors have methylated hexahydro-picolinic and -nicotinic acids by means of formaldehyde.

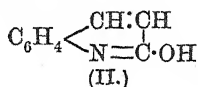
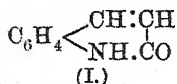
Nicotinic and picolinic acids are obtained by the oxidation of technical picoline by a process which is described in detail, and these acids are reduced by the Paal-Skita method.

Hexahydronicotinic acid (nipecotinic acid) forms a hydrochloride, m. p. 280° (decomp.), which is unstable in solution, especially at 70—80°. 1-Methylnipecotinic acid (1-methylpiperidine-3-carboxylic acid) is an unstable substance which has not been obtained crystalline, but is characterised by a methyl ester, b. p. 90—93°/15 mm. This is a strongly alkaline, limpid, highly refractive, viscous oil which provokes to sneezing, and forms an *aurichloride*, in bundles of stout, yellow prisms, m. p. 105°.

Hexahydronicotinic (pipecolic) acid forms an acetate, m. p. 219° (decomp.), and ethyl 1-methylpipecolate (1-methylpiperidine-2-carboxylate) is a limpid, refractive syrup, b. p. 92—96°/11 mm. J. C. W.

Anhydroximes. II. ROBERT EVSTAFIEFF ROSE and WINFIELD SCOTT, Jun. (*J. Amer. Chem. Soc.*, 1917, 39, 273—279. Compare A., 1911, i, 372).—*o*-Aldehydobenzoic anhydroxime when reduced by zinc in acetic acid gives phthalimidine, m. p. 150—151°, which is in part further reduced to dihydroisoindole. *o*-Acetylbenzoic anhydroxime under similar conditions gives 1-methylphthalimidine and 1-methyldihydroisoindole. 1-Methylphthalimidine when boiled with acetic anhydride and potassium acetate gives an *acetyl* derivative, colourless needles, m. p. 71°. β -Ketobutyric anhydroxime [3-methylisooxazalone] when reduced with zinc and acetic acid yields ammonia and butyric acid, there being no evidence of the formation of a tetratomic ring compound. W. G.

Nitration of Quinolone and Carbostryl Ethers. ADOLF KAUFMANN and VICTOR PETHEOU DE PETHERD (*Ber.*, 1917, 50, 336—344).—The nitration of the lactam form of "carbostryl" (I), better known as quinolone, and of its *N*-alkyl derivatives, and of *O*-ethers of the lactim type (II), is described. It is shown that



the first nitro-group enters position 6 in each case, and that quinolone and 1-alkylquinolones ultimately yield 3:6:8-trinitro-derivatives, whereas the carbostryl ethers only give 6:8-dinitro-compounds.

Quinolone is most readily obtained by converting 1-methylquinolone into 2-chloroquinoline (Fischer, A., 1898, i, 383) and boiling this with dilute hydrochloric acid. When treated with cold con-

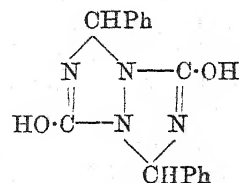
centrated nitric acid, this yields 6-nitroquinolone, m. p. 280° (the 6-nitrocarbostyryl of Friedländer, A., 1885, 1139, and Cohn and Springer, A., 1903, i, 493). With a warm mixture of fuming nitric and sulphuric acids, however, the product is 3:6:8-*trinitroquinolone*, which crystallises in stellate groups of yellow needles, decomp. 176° , and forms *molecular compounds* with acenaphthene (red needles, decomp. 188°), α -naphthol (red spikes, detonating at 200°), and β -naphthol (red crystals, decomp. 206°). It is difficult to regulate the nitration so as to get a dinitro-compound, but 6:8-dinitroquinolone, white crystals, m. p. 218° , and the less soluble 3(?) : 6-dinitroquinolone, pale yellow needles, m. p. 253° , have been obtained in this way. The position of the 6- and 8-nitro-groups is determined by the fact that the above 3:6:8- and 6:8-compounds yield 3:5-dinitroanthranilic acid (leaflets, m. p. 268°) on oxidation with 1% permanganate.

1-Methylquinolone yields 3:6:8-*trinitro-1-methylquinolone*, m. p. 213° (compare Decker, A., 1901, i, 655). The positions of the nitro-groups are proved by the oxidation of the substance to 3:5-dinitro-2-methylaminobenzoic acid, delicate, yellow leaflets, m. p. 228 — 229° , which yields the known 3:5-dinitrosalicylic acid on warming with sodium carbonate.

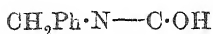
Carbostyryl methyl ether is readily obtained by the action of sodium methoxide solution on 2-chloroquinoline. Unlike 1-methylquinolone, it forms a *picrate*, which crystallises in glistening, yellow needles, m. p. 170 — 171° . It yields 6-nitro-2-methoxyquinoline, white spikes, m. p. 189 — 190° , when mildly nitrated (obviously the nitromethylcarbostyryl, m. p. 181° , described by Feer and Koenigs, A., 1885, 1235). The nitro-group affords some protection to the methyl group against hydrolysis, for the compound must be heated with hydrochloric acid under pressure in order to convert it into 6-nitroquinolone. 6:8-Dinitro-2-methoxyquinoline is obtained by warming the mono-derivative with nitrating mixture, in white needles, m. p. 206° , and this may be hydrolysed to the above 6:8-dinitroquinolone.

Carbostyryl ethyl ether, b. p. 266° , $130^{\circ}/12$ mm., forms a *picrate*, $1H_2O$, yellow leaflets, m. p. 147° . 6-Nitro-2-ethoxyquinoline crystallises in white needles, m. p. 156 — 158° . J. C. W.

The Use of Cyanic Acid in Glacial Acetic Acid. II. The Addition of Cyanic Acid to Benzaldazine. J. R. BAILEY and N. H. MOORE (*J. Amer. Chem. Soc.*, 1917, **39**, 279—291. Compare



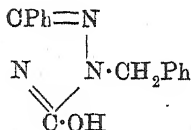
hyde it gives what is probably an additive product in the form of a gelatinous mass, which, however, gives up its formaldehyde again on drying. The "triazolotriazole" gives a *diacetyl* derivative, slender needles, m. p. 167° (decomp.). When dissolved in 10% aqueous potassium hydroxide and distilled with steam the "triazolo-



triazole" is decomposed, giving benzaldehyde, which distils over, and there is left in the flask benzaldsemicarbazone, which is insoluble in the alkali, and a compound, $\text{C}_{15}\text{H}_{13}\text{ON}_3$, short needles, m. p. 208°, which is precipitated on acidifying the solution with hydrochloric acid. This compound is con-

sidered to have the annexed constitution, and is isomeric with the triazole, m. p. 228° (see below).

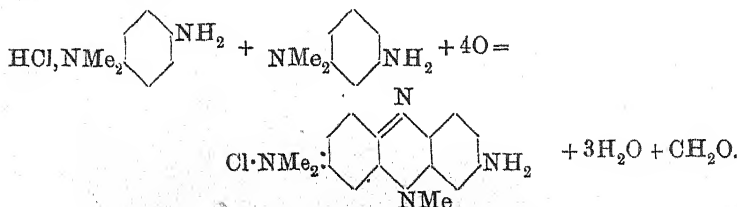
When the "triazolotriazole" is boiled with concentrated hydrochloric acid it slowly dissolves, being hydrolysed to benzaldehyde, hydrazine, and hydrazodicarbonamide. When oxidised with concentrated nitric acid at below 10° it gives 5-hydroxy-3-phenyl-1:2:4-triazole, m. p. 321—322° (decomp.) (compare Young and Witham, T., 1900, 77, 226).



When benzylbenzylidenesemicarbazone is heated in a sealed tube with alcoholic ferric chloride for four hours at 125—135°, it is oxidised, giving 5-hydroxy-3-phenyl-1-benzyl-1:2:4-triazole (annexed formula), m. p. 228°, which is isomeric with the compound, m. p. 208°, described above.

W. G.

Tetramethyldiaminophenazine. P. KARRER (*Ber.*, 1917, 50, 420—421). F. KEHRMANN and G. FALCONNIER (*ibid.*, 421—422).—The compound which Karrer obtained by oxidising a mixture of dimethyl-*m*- and dimethyl-*p*-phenylenediamines (*A.*, 1916, i, 847) was not an azine but a dye of the safranine type, produced according to the scheme:



Karrer himself is led to doubt his earlier suggestion because true tetramethyldiaminophenazine has since been prepared by his colleague, Bauer, who will report on it. Kehrmann and Falconnier point out that Karrer's compound is insoluble in ether and contains a diazotisable amino-group.

J. C. W.

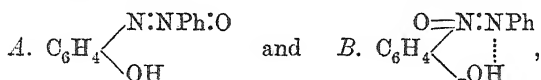
Nitrosoarylhydroxylamines. VIII. Hydroxyazoxy-compounds and Nitrosophenylhydroxylamines. OSKAR BAUDISCH (*Ber.*, 1917, 50, 333—336).—Most of the peculiarities of *o*-hydroxy-

azo-, -azoxy-, or -nitrosoarylhydroxylamino-compounds can be explained by formulæ which involve the phenolic hydroxyl group in union by residual affinities with one of the nitrogen atoms.

Thus, the formula $C_6H_4 \begin{array}{c} \diagup N:NPh \\ \vdots \\ \diagdown OH \end{array}$ would explain why *o*-azophenol

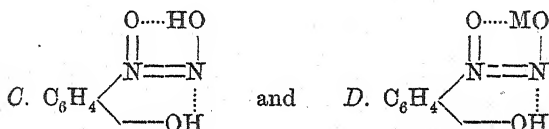
only combines with one molecule of ammonia and is not oxidised by silver oxide, whereas *p*-azophenol absorbs two molecules of ammonia and is readily oxidised to a quinoneazine, and *m*-azophenol is not oxidisable and combines with an intermediate amount of ammonia (Willstätter and Benz, A., 1906, i, 990).

The formula *A* for normal *o*-hydroxyazoxybenzene and *B* for the *iso*-compound (Bamberger, A., 1900, i, 531), explain the lack of



tinctorial properties, the resistance towards permanganate, and the insolubility in ammonia or sodium carbonate of the *iso*-compound, and also why 2:2'-dihydroxyazoxybenzene exists in only one form (following abstract).

Similarly, the formulæ *C* and *D* for nitroso-*o*-hydroxyphenylhydroxylamine and its salts, explain the influence of the position



of the hydroxyl group on the stability of these compounds (this vol., i, 331).

The importance of this internal salt formation between the azo- and *o*-hydroxy-groups is obviously of great interest in connexion with *o*-hydroxyazo-dyes. J. C. W.

2:2'-Dihydroxyazoxybenzene. OSKAR BAUDISCH and J. HAFTKA (*Ber.*, 1917, 50, 332).—This compound has been prepared for comparison with 2-hydroxyazoxybenzene (Bamberger, A., 1900, i, 531) and the 3:3'- and 4:4'-dihydroxyazoxybenzenes (A., 1904, i, 238; A., 1888, 1287).

o-Hydroxylaminophenyl *p*-toluenesulphonate (A., 1912, i, 442) is shaken with silver oxide in ethyl acetate mixed with anhydrous sodium sulphate, and then the green filtrate is boiled with a further portion of the ester until the dark brown liquid no longer reduces Fehling's solution. 2:2'-*Di-p*-toluenesulphonoxazoxybenzene is thus obtained, in straw-yellow crystals, m. p. 145—147°, and this yields 2:2'-*dihydroxyazoxybenzene* on hydrolysis, in pale yellow, transparent rhombohedra, m. p. 154—155°. Unlike 2-hydroxyazoxybenzene, this compound exists in only one form, but, like it, it yields a brown copper salt. J. C. W.

Leucine Anhydride, a Product of the Hydrolysis of Protein by Water at High Temperatures. S. S. GRAVES and J. T. W. MARSHALL [with H. W. ECKWEILER] (*J. Amer. Chem. Soc.*, 1917, **39**, 112—114).—When casein is heated with water in an autoclave at 180—200° for sixteen hours and the product extracted with ether, a crystalline compound, m. p. 272°, is obtained and has been identified as leucine anhydride. Under similar conditions leucine itself only gives a trace of the anhydride, whilst leucylleucine gives more than a 90% yield of the anhydride. A number of proteins have been similarly treated, and the yields of leucine anhydride obtained were: casein, 1.5%; egg-albumin, 1.2%; edestin, 1.2%; Witte's peptone, 1.0%; silk, 0.09%; gelatin, 0.04%. W. G.

Auxo-amylases. ELBERT W. ROCKWOOD (*Proc. Amer. Soc. Biol. Chem.*, 1916, xxxiv—xxxv; *J. Biol. Chem.*, 1917, **29**).—The accelerating influence of α -amino-acids on the hydrolysis of starch by ptyalin is not lost by substituting other radicles for the hydrogen of the amino-group. Thus, hippuric acid and glycine have a similar accelerating action on ptyalin. The substitution of a carboxyl radicle for the amino-group is attended with complete loss of activating power. Introduction of a sulphonic acid radicle also neutralises the effect produced by the amino-group; thus acid amides, including urea, and sulphanilic acid are devoid of accelerating power. The position of the amino-group, as in the isomeric aminobenzoic acids, does not modify the accelerating action on ptyalin. Compounds of amino-acids, like the proteins, also activate the enzyme.

As far as the author has investigated, pancreatic diastase and ptyalin are similarly affected by amino-acids. H. W. B.

Formation of Urea by Arginase and the Specificity of its Action. A. CLEMENTI (*Archiv di Fisiol., Florence*, 1916, **14**, 207—228; from *Physiol. Abstr.*, 1917, **1**, 508).—Hepatic arginase cannot resolve guanidylglycine into glycine and urea. Neither hepatic nor renal arginase splits creatine into sarcosine and urea. Arginase is also unable to split guanidylglycylglycine into glycylglycine and urea. G. B.

The Measurement of Oxidation Potential and its Significance in the Study of Oxydases. G. B. REED (*Bot. Gaz.*, 1916, **61**, 523—527).—In studying the rôle of plant oxydases, the author has tried with success a new method of following the progress of the oxidation reactions, namely, by measuring the oxidation potential of the solutions entering into the reactions. The apparatus consists essentially of a reaction cell in which is placed the solution to be tested with a platinum electrode dipping into the solution. The other half of the cell is a standard calomel electrode connected with the reaction cell by a syphon. Measurement of the potential of the cell is made by the Poggendorf compensation method. L. M. U.

Preparation of Derivatives of Arsenobenzene containing Nitrogen. FARBW. VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 294276; from *J. Soc. Chem. Ind.*, 1917, **36**, 403).—3:5-Dinitro-4-dialkylaminobenzene-1-arsinic acids are treated with reducing agents. The preparation of *tetramethylhexaminoarsenobenzene*, *tetraethylhexaminoarsenobenzene*, and *dipiperidinotetraminoarsenobenzene hydrochlorides* is described. The products have a higher therapeutic value and a more pronounced action on certain parasites than the corresponding dialkyl compounds. H. W.

Preparation of Thiocarbamide Compounds of Arsanilic Acid, its Homologues and Derivatives. H. THOMS (D.R.-P., 294632; from *J. Soc. Chem. Ind.*, 1917, **36**, 403).—Arsanilic acid or a homologue or derivative is treated with allylthiocarbimide, using methyl alcohol as solvent. The products have the combined therapeutic action of allyl and arsenic compounds, without exhibiting the poisonous character of the latter. The compound of allylthiocarbimide and arsanilic acid has m. p. 185° (decomp.), and is almost insoluble in water and alcohol, sparingly soluble in methyl alcohol. The corresponding compound of methylarsanilic acid darkens and intumesces at 170° without melting. H. W.

Physiological Chemistry.

Micro-titration of Ammonia, with some Observations on Normal Human Blood. GEORGE D. BARNETT (*J. Biol. Chem.*, 1917, **29**, 459—462).—The author's procedure differs from the usual aeration-titration method in the employment of a micro-burette and 0.005*N*-alkali. By this method the amount of ammonia in fresh normal human blood is found to be about 0.03 mg. per 100 c.c., which increases rapidly on keeping and reaches 0.10 mg. within thirty minutes. H. W. B.

Nature of the Sugar in the Blood. HUGH MCGUIGAN (*Proc. Amer. Soc. Biol. Chem.*, 1916, xx-xxi; *J. Biol. Chem.*, 1917, **29**).—The author calls attention to the existence of a polysaccharide in the blood of the nature of dextrin, and suggests that estimations of the sugar in the blood should be made before and after hydrolysis in order that the ratio of the free to combined or complex sugar may be determined. H. W. B.

Carbohydrate Metabolism. XIV. Influence of Administration of Alkali on the Sugar Content of the Blood in Relation to the Acid-Base-producing Properties of the Diet. XV. Influence of Acid-forming and Base-forming Diets on the Sugar Content of the Blood. LOUISE McDANELL and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1917, **29**, 227—232, 233—243).—The authors find that in the normal rabbit the sugar

content of the blood is not significantly changed by variations in the acid-base content of the diet which are sufficient to cause a marked change in the hydrogen-ion concentration of the urine. The intravenous injection of dilute sodium carbonate solution into the rabbit does not usually lower the sugar content of the blood, although it sometimes has this effect (compare Underhill, A., 1916, i, 685). Any hypoglycaemia produced must apparently be due to some other cause than the mere increase in the alkalinity of the blood. H. W. B.

Partition of Non-protein Nitrogen in the Blood of Fresh-water Fish. D. WRIGHT WILSON and EDWARD F. ADOLPH (*J. Biol. Chem.*, 1917, **29**, 405—411).—The authors have estimated the total non-protein nitrogen, urea, ammonia, amino-nitrogen, creatinine, and creatine in the whole blood and in the plasma of several species of fresh-water fish, including ganoids and teleosts. The urea content of the bloods is unusually low, and the concentration in the plasma is less than that in the corpuscles. The major part of the total non-protein nitrogen of the blood consists of amino-nitrogen, and here also the corpuscles contain more than the plasma. The authors suggest that possibly in the fish nitrogen is excreted in the form of amino-acid instead of urea. Creatine occurs in unusually large proportions, especially in the plasma. H. W. B.

Amino-acid Nitrogen Content of the Blood of Various Species. JOSEPH C. BOCK (*J. Biol. Chem.*, 1917, **29**, 191—198. Compare this vol., ii, 159).—The amount of amino-acid nitrogen in the blood of various animals is constant for each species. The amino-acid nitrogen of bird's blood is about three times as high as that of a mammal. The corpuscles usually contain more amino-acids than the serum.

There is about 7 mg. of amino-acid nitrogen in 100 c.c. of normal human blood. Sex does not appear to influence this amount, but the figures for placental blood are distinctly higher. Considerable variations, ranging from 4.5 mg. to 30 mg. per 100 c.c. of blood, occur in pathological conditions, higher figures being observed particularly in nephritis and uraemia. H. W. B.

Creatine and Creatinine in Whole Blood and Plasma. D. WRIGHT WILSON and E. D. PLASS (*J. Biol. Chem.*, 1917, **29**, 413—423).—The authors describe a modification of Folin's method for estimating the preformed creatinine and total creatinine (creatinine+creatine) in the whole blood, in which the blood proteins are removed by heating in dilute acetic acid solution, followed by treatment with aluminium hydroxide. Folin's method is regarded as satisfactory when applied to serum or plasma, but not when used for the whole blood.

By their method, the authors find from 2 to 5.2 mg. of total creatinine per 100 c.c. in the whole blood of various animals, which were presumably normal. Human blood contains about 3 mg. per 100 c.c. These figures are much lower than practically all data given by other workers (compare Folin and Denis, A., 1914, i, 764). Larger amounts of creatine are found in the plasma of infants than

in that of adults. The blood plasmas of the pig and of the hen contain even larger quantities. Corresponding with these high figures, there is a greater excretion of creatine in the urine. A characteristic relationship appears to exist between the concentration of creatine in the plasma and the amount eliminated in the urine.

H. W. B.

Fibrin Excretion under the Influence of an Electric Current. E. HEKMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, 19, 900—903).—The clotting of blood consists in the formation of a fibrin gel, which is insoluble in water, but may be transformed into a sol by the action of very dilute solutions of acid or alkali hydroxide. By neutralising the acid or alkali sols the fibrin separates out again in gel form. The same result is obtained when an electric current is passed through the sols. Coagulation occurs at the positive electrode with alkali sols and at the negative with acid sols. The fact that natural fibrin sols also show gel formation at the positive electrode under the influence of a current is considered to show that in the clotting of blood the fibrin is converted from the alkali sol into the gel condition.

H. M. D.

The Digestibility of Bread. II. Salivary Digestion of Erythrodextrin in Vitro. J. C. BLAKE (*J. Amer. Chem. Soc.*, 1917, 39, 315—320. Compare A., 1916, i, 578).—The digestion of erythrodextrin by ptyalin is a unimolecular reaction, the optimum temperature for which is 51°. At the ordinary temperature the temperature-coefficient is relatively small. At 65° the enzyme is killed. When the ratio of substrate to enzyme is very large, the digestion becomes disproportionately slow, this ratio being constant for different concentrations. It is suggested that it represents a union of enzyme and the substrate prior to hydrolysis. Maltose only exerts a relatively small retarding influence on this digestion, the influence varying directly with the concentration of the maltose.

W. G.

The Assumed Destruction of Trypsin by Pepsin and Acid. II. Observations on Animals. J. H. LONG and MARY HULL (*J. Amer. Chem. Soc.*, 1917, 39, 162—174. Compare A., 1916, i, 770).—Experiments were carried out on dogs to determine the combined effect of pepsin and hydrochloric acid on trypsin, under conditions which correspond with those obtaining in the human stomach at times, when the latter ferment is ingested. The trypsin was fed either with or without meat and the stomach contents were secured by one of four methods, namely, (a) by means of a tube after the ligation of the pylorus, the organ thus constituting a closed pouch in which the secretion followed normally for a time; (b) from the normal, open stomach by the tube applied at the proper interval after the ingestion of food and trypsin; (c) by means of a gastric fistula made in the normal organ and opened from time to time for the withdrawal of the contents; (d) from a false stomach or Pavlov pouch constructed from the normal organ.

In all cases the secretion of pepsin and acid was abundant, and thus the conditions for the persistence of trypsin were not favourable. In the larger number of experiments, however, the trypsin was not destroyed by the pepsin-acid combination where sufficient protein was present to reduce the acid concentration to a certain value. Only when the acid was in excess of the pepsin did the trypsin seem to be destroyed or greatly weakened. It is possible, therefore, that some tryptic digestion may occur in the human stomach when the free acid is very low from protein combination.

W. G.

Activation of Pancreatic Lipase by Cholates. (MLLE.)

J. A. DE JONGE (*Arch. Néerland. Physiol.*, 1917, 1, 182—197).—The extent of activation of pancreatic lipase by sodium cholate depends on the age of the pancreatic extract and appears to vary rhythmically as the age of the extract increases. A pancreatic extract, the activity of which is increased by the addition of sodium cholate, may at the end of a week have entirely lost the capacity for being thus activated. If this extract is kept for another week, it is found that the addition of cholate again begins to exert an activating action, and at the end of the second week the activation produced by the cholate may be greater than that observable with the original extract. At the end of the third week the activating capacity may have again vanished, and so on. A satisfactory explanation of this phenomenon, which was repeatedly observed, is not given by the author.

The addition of gum arabic to the pancreatic extract produces an activating effect owing to its emulsifying action on the substrate. This action is found to be independent of the age of the pancreatic extract. The specific action of sodium cholate is therefore different from that of gum arabic; it is not concerned with the emulsification of the substrate, but with a true activation of the enzyme, lipase (compare Donath, A., 1907, ii, 975).

H. W. B.

Effect of Bile and Bile Salts on the Reaction between Oleic Acid and Sodium Hydrogen Carbonate. F. B. KINGSBURY

(*J. Biol. Chem.*, 1917, 29, 367—380).—The author describes experiments which demonstrate that the reaction between oleic acid and sodium hydrogen carbonate proceeds further in the presence than in the absence of bile, so that the presence of bile in the small intestine makes possible a much greater soap formation from the fatty acids liberated during digestion than could otherwise be the case with an alkali as weak as sodium hydrogen carbonate.

Attention is drawn to the erroneous statement in many text-books of physiological chemistry that the alkali of the small intestine, available for the neutralisation of the fatty acids, is sodium carbonate, instead of sodium hydrogen carbonate.

H. W. B.

Vitamine Content of Brewers' Yeast. ATHERTON SEIDELL

(*J. Biol. Chem.*, 1917, 29, 145—154).—By feeding experiments it is shown that in the case of pigeons the vitamine deficiency of an

exclusive diet of polished rice is just replaced by daily doses of 0.5—1.0 c.c. of the clear filtrate from autolysed brewers' yeast. The deficiency is not replaced by doses of dried freshly pressed yeast approximately equivalent to 1 c.c. doses of autolysed yeast. Yeast which is autolysed before drying is more efficient than ordinary dried yeast.

On the assumption that the nitrogenous material removed by fullers' earth from the autolysed yeast filtrate consists of vitamine, it is calculated that a grown pigeon requires daily somewhat less than 1 mg. of vitamine. The diet, therefore, of a pigeon, and possibly also of man, must contain about 0.0033 per cent. of vitamine.

H. W. B.

Maize as a Source of Protein and Ash for Growing Animals. ALBERT G. HOGAN (*J. Biol. Chem.*, 1917, 29, 485—493).—Maize is deficient in calcium, tryptophan, and lysine. When these substances are added to the diet, the growth of rats is well maintained.

H. W. B.

Dietary Deficiencies of the White Bean, *Phaseolus vulgaris*. E. V. MCCOLLUM, N. SIMMONDS, and W. PRITZ (*J. Biol. Chem.*, 1917, 29, 521—536).—The proteins of the white bean appear to have a low biological value. The carbohydrates in the bean are also particularly liable to undergo fermentation in the digestive tract, with the liberation of large quantities of gas. In some rats fed on the beans the distension of the intestinal tract with gas was apparently the direct cause of death. The beans are also deficient in the accessory substance, "fat soluble A," and in suitable inorganic constituents; but they are rich in "water soluble B," and may therefore be employed in small quantities to supplement food materials in which this accessory is missing or deficient. The addition of 25% of the beans to a diet containing adequate protein, salts, carbohydrates, and butter-fat (for fat soluble A) induces perfectly normal growth in rats with the production of normal litters of young, which in their turn make adequate growth on the same diet.

H. W. B.

The Chemical Individuality of Tissue Elements and its Biological Significance. P. A. LEVENE (*J. Amer. Chem. Soc.*, 1917, 39, 828—836).—An address delivered to a meeting of the Chemical Section of the A.A.A.S. in New York.

W. G.

Ferments of Human Cerebro-spinal Fluid. ERICH LESCHKE and LUDWIG PINCUSOHN (*Deut. med. Woch.*, 1917, 43, 8—9).—Cavazzani's observations on the presence of glycolytic and amyolytic (diastatic) ferments were confirmed polarimetrically. In four cases of diabetes the glycolytic ferment was absent. The diastatic ferment is present in health and in various diseases, but only in small amount. Protective ferments (*Abwehrfermente*) never pass from the blood into the cerebro-spinal fluid, which circumstance the authors consider an important argument in favour of the origin

of the fluid as a specific secretion and against the view that it is of the nature of lymph or transudate. G. B.

Autolysis. V. Influence of Bile on Autolysis. H. C. BRADLEY and JOSEPH TAYLOR (*J. Biol. Chem.*, 1917, **29**, 281—288. Compare Tatum, A., 1916, i, 863).—The authors find that bile does not accelerate the autolysis of liver, spleen, kidney, thymus, or heart muscle. The rapid disintegration of cellular tissues when placed in bile observed by Tatum (*loc. cit.*) must therefore be due to cytolysis as distinct from autolysis. H. W. B.

Carbohydrate Metabolism. XVIII. Relation of Diet to the Glycogen Content of the Liver. LOUISE McDANELL and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1917, **29**, 255—263).—Although a large storage of glycogen in the liver of a rabbit may take place on an acid-producing diet, a still larger quantity is usually formed on a diet which yields a basic ash. The authors draw the conclusion that an excess of alkali favours the accumulation of glycogen. H. W. B.

Active Constituent of the Thyroid ; its Isolation, Chemical Properties, and Physiological Action. E. C. KENDALL (*Proc. Amer. Soc. Biol. Chem.*, 1916, xxix—xxx; *J. Biol. Chem.*, 1917, **29**).—Primary cleavage of the thyroid proteins yields acid-soluble and acid-insoluble compounds. The active iodine compound is included in the latter, and is isolated by taking advantage of the solubility of its barium compound in barium and sodium hydroxides. It is finally obtained in microscopic needles from alkaline alcohol by precipitation with acetic acid. The free base contains 65% of iodine, whilst the sulphate, which is soluble in alcohol, contains 60% of iodine and has a molecular weight of 586.

A dose of 0.125 to 0.25 mg. of the substance is sufficient in cases of cretinism, whilst amounts up to 2 mg. daily are tolerated in the human subject. Excessive doses administered to animals evoke symptoms of hyperthyroidism and eventually cause death.

H. W. B.

Composition of Adipocere. R. F. RUTTAN and M. J. MARSHALL (*J. Biol. Chem.*, 1917, **29**, 319—327).—A specimen of adipocere from a pig has the following composition: Palmitic acid, 67.52%; other fatty acids, 24.34%; calcium soaps, 4.41%; fats and unsaponified matter, 2.24%; and protein, 0.665%. Besides palmitic, stearic, and oleic acids, two hydroxystearic acids were isolated and identified, namely, *l*-hydroxy- and *θ*-hydroxy-stearic acids. These are characteristic of adipocere, and are probably derived from a portion of the oleic acid in the original fat by hydration. Neither margaric nor hydroxymargaric acids were detected; ammonium and other soluble soaps were also absent. It is evident that adipocere is the residue of the pre-existing fats of animals, and is composed almost entirely of the insoluble fatty acids left after the slow hydrolysis of the fats in the wet ground.

The protein matter has almost entirely disappeared, as well as the glycerol and soaps resulting from the hydrolysis of the fats.

The fatty acids, traces of fats, etc., soluble in ether constituted 94.1% of the adipocere, and gave the following constants: D^{100} 0.8436, n_D^{25} 1.436, and m. p. 60—63°. H. W. B.

Bioluminescence. II. Luciferin in Luminous Bacteria.
III. Action of Oxydases. E. NEWTON HARVEY (*Amer. J. Physiol.*, 1916, **41**, 449—453, 454—463; from *Physiol. Abstr.*, 1916, **1**, 376).—II. R. Dubois's thermostable, oxidisable substance luciferin and his thermolabile enzyme-like substance luciferase, occur in the luminous organs of the mollusc *Pholas*, the beetle *Pyrophorus*, and in American fireflies. Impure luciferin can be prepared by precipitating luminous bacteria with alcohol, and will give light when mixed with firefly luciferase. The luciferase of bacteria is probably an endoenzyme, and has not yet been isolated from them. Oxydases for pyrogallol, guaiacum, etc., are also in an endoenzyme condition. Oxygen is necessary for light production; in the absence of oxygen, luciferase decomposes luciferin without the production of light. Firefly luciferase is readily destroyed by ether or chloroform, so differing from vegetable oxydases. Luciferin is not readily destroyed by these reagents. Luciferin of bacteria or firefly gives no light with potato-juice oxydase, with or without the addition of hydrogen peroxide.

III. Pyrogallol, even in very low concentration, gives off a yellow light about equal to that of luminous bacteria when oxidised by blood or plant oxydases in presence of hydrogen peroxide; the hydroxy- and amino-phenols do not act thus. Potassium ferricyanide, potassium permanganate, or ferric chloride may replace the oxydase. The light is brighter at 10° than at 0°. The light production is inhibited by potassium cyanide or by dilute acids and alkalis. Ether and chloroform have no effect. The oxydase is not a true catalyst, but transfers oxygen from the hydrogen peroxide to the pyrogallol. This mimics light production by luminous animals very closely. G. B.

Bioluminescence. IV. In Cypridina Hilgendorffii (Japanese Ostracod Crustacean); V. In Firefly; VI. In Cavernularia Haberi (Japanese Pennatulid). E. NEWTON HARVEY (*Amer. J. Physiol.*, 1917, **42**, 318—341, 342—348, 349—358; from *Physiol. Abstr.*, 1917, **2**, 4).—IV. The luminous secretion comes from the upper lip. It gives the luciferin-luciferase reaction. Luciferase is not an enzyme, as Dubois thinks, but is the source of light. The new name *photogenin* is proposed, and *photophlein* (light assister) is the new name given to luciferin. Oxygen is necessary. Both substances pass through a Chamberland filter and dialysing membranes; they are adsorbed by bone-black, and may be dried and extracted with ether without impairment. One part in 1700 millions of water gives visible light even at 0°. Photophlein occurs throughout the body, but photogenin in the luminous

organ only. The latter is the more stable, but is destroyed at 70°. Many other details are given.

V. The photogenin of the firefly is not so stable, and is destroyed at 42° and by fat solvents.

VI. Here the light arises from a slime secreted by the outer surface of the colony; the light is emitted by granules, which will pass through an alundum, but not a Chamberland filter, and do not dialyse; nor are they adsorbed by bone-black. The colony gives light on electrical stimulation. No light occurs in the absence of oxygen; the juice reduces methylene-blue and contains peroxydases and catalase. This animal does not give the photogenin-photophlein reaction but a faint light is obtained with a non-luminous *Cavernularia* juice (photogenin) and photophlein from *Cypridina* or firefly. G. B.

Preparation of Scyllitol from Dog-fish (*Scyllium canicula*). OTTO ROSENHEIM (*Proc. Physiol. Soc.*, vii—viii; *J. Physiol.*, 1917, 51).—This optically active inositol, which is limited to Elasmobranch fishes, may be fairly readily prepared from the common dog-fish by extraction with acetone; yield, 1 gram from 10 kilos. G. B.

Adenine and Guanine in Cows' Milk. CARL VOEGTLIN and C. P. SHERWIN (*Proc. Amer. Soc. Biol. Chem.*, 1916, vi; *J. Biol. Chem.*, 1917, 29).—The authors have isolated 500 mg. of adenine and 100 mg. of guanine from the protein-free residue from 100 litres of a mixed sample of cows' milk. These two bases have not hitherto been recognised in milk. H. W. B.

Acid-base Equilibrium in the Body. JOHN HOWLAND and W. MCKIM MARRIOTT (*Proc. Amer. Soc. Biol. Chem.*, 1916, v—vi; *J. Biol. Chem.*, 1917, 29).—The administration of hydrochloric acid in man leads to an increase in the titratable acid (A) and a proportionate increase in the ammonia (B) excreted in the urine, the ratio A:B remaining constant. In the case of sodium dihydrogen phosphate, the titratable acid is increased, but the ammonia is unchanged, so that the ratio A:B is greatly increased. Administration of phosphate mixtures of the same hydrogen ion concentration as that of normal blood is followed by a slight increase in the titratable acid and a distinct diminution in the excreted ammonia. These results are in accord with the clinical data, since, in cases of nephritis, which are accompanied by a retention of dihydrogen phosphate, the acidosis is attended with a low excretion of ammonia. In these cases, therefore, ammonia estimations do not give trustworthy information regarding the state of acidosis which may be existing. H. W. B.

Hourly Elimination of certain Urinary Constituents during Brief Fasts. ISAAC NEUWIRTH (*J. Biol. Chem.*, 1917, 29, 477—484).—The amounts of uric acid, creatinine, and total nitrogen passed hourly in the urine of a young man during a

twenty-seven hours' fast vary considerably during the day. The last meal is taken at 6 p.m., and during the following morning there is a marked decline in the uric acid output, which becomes more gradual during the afternoon. A close correspondence occurs in the rise and fall of uric acid and total nitrogen. The creatinine output shows marked variations from hour to hour from unknown causes. It reaches a minimum towards the end of the afternoon.

H. W. B.

Diurnal Variations in Creatine Excretion. W. DENIS [with ANNA S. MINOT] (*J. Biol. Chem.*, 1917, **29**, 447—451).—The analyses of the urines of several patients suffering from various diseases show that whilst the day urines contain considerable quantities of creatine, the urines passed during the night are practically free from creatine. By collecting the urine more frequently, it is found that on a strictly creatine-free diet, the maximum excretion of creatine occurs about two hours after the most substantial meal of the day. This result indicates that creatine is of exogenous origin and that its excretion is directly dependent on the intake of food.

H. W. B.

Rate of Excretion of Urea. III. Effect of Changes in the Concentration of Urea in the Blood on the Rate of Excretion of Urea. IV. Effect of Changes in the Volume of Urine on the Rate of Excretion of Urea. T. ADDIS and C. K. WATANABE (*J. Biol. Chem.*, 1917, **29**, 391—398, 399—404. Compare A., 1916, i, 352, 864).—The rate of excretion of urea increases with increasing concentration of urea in the blood. A curve is constructed by the authors from data obtained from numerous persons showing the relation between these two factors.

After abstention from food and water, the drinking of large quantities of water is followed by an increase in the volume of urine and by a synchronous acceleration of the rate of excretion of urea, which cannot be accounted for on the basis of changes in the concentration of urea in the blood. The increased rate of excretion does not appear, however, to be the result of the increased volume of urine, since the degree of increase above the normal in the rate is quantitatively independent of the degree of increase in the volume. The authors conclude, therefore, that the rate of excretion of urea is not appreciably affected by changes in the volume or in the concentration of urea in the urine.

H. W. B.

Experimental Glycosuria. XI. Retention of Dextrose. J. J. R. MACLEOD, M. E. FULK, J. H. DAVIS, and R. W. SCOTT (*Amer. J. Physiol.*, 1917, **42**, 193—213; from *Physiol. Abstr.*, 1917, **2**, 38).—Injection of large doses of dextrose into the portal and iliac veins and vena cava shows that in dogs the sugar-retaining power of the liver is about equal to that of the hind-limb muscles. Large amounts of dextrose raise the H-ion concentration of the blood; injection of sodium carbonate then lowers both the

H-ion concentration and the sugar content, but whether the liver or the muscles are responsible for this sugar retention is not clear.

G. B.

Carbohydrate Metabolism. XIX. Influence of the Intravenous Injection of Sodium Carbonate on the Hyperglycæmia and Glycosuria following the Subcutaneous Administration of Dextrose. LOUISE McDANELL and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1917, 29, 265—272).—The results of these experiments on rabbits are so variable that the authors are unable to draw any definite conclusion.

H. W. B.

Carbohydrate Metabolism. XX. Mechanism of Salt Glycosuria. LOUISE McDANELL and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1917, 29, 273—280).—The results of previous work are confirmed (Underhill and Closson, A., 1906, ii, 243). The authors consider that the absence of concomitant hyperglycæmia justifies the conclusion that saline glycosuria is due to an increased permeability of the kidney (compare Hirsch, A., 1915, i, 744).

H. W. B.

Carbohydrate Metabolism. XVI. Relation of Adrenaline Glycosuria to Dosage and to the Character of the Diet. XVII. Influence of the Intravenous Injection of Sodium Carbonate on Adrenaline Hyperglycæmia and Glycosuria. LOUISE McDANELL and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1917, 29, 245—250, 251—254).—Rabbits on a mixed diet excrete larger amounts of sugar after the administration of small amounts of adrenaline than when maintained on either an acid-producing diet or one yielding a basic ash. Intravenous injection of sodium carbonate reduces the influence of the minimum effective dose of adrenaline (0.3 mg. of adrenaline per kilo. of body-weight in the case of a normal rabbit), but it does not entirely prevent the occurrence of hyperglycæmia and glycosuria. Apparently, with the smaller dose of adrenaline, hyperglycæmia and glycosuria are diminished relatively less by sodium carbonate than when larger doses of adrenaline are employed (compare Underhill, A., 1916, i, 685).

H. W. B.

Bence-Jones Proteinuria. II. A. E. TAYLOR, C. W. MILLER, and J. E. SWEET (*J. Biol. Chem.*, 1917, 29, 425—435. Compare Taylor and Miller, A., 1916, i, 584).—Further experiments are described in which the effect of the injection of the Bence-Jones protein into the animal body has been ascertained. Normal dogs can utilise or catabolise moderate quantities of Bence-Jones protein injected intravenously or subcutaneously, but a limit is soon reached beyond which the protein is promptly excreted in an unchanged condition. In dogs suffering from moderate uranium poisoning this power of utilisation is absent, and the Bence-Jones protein is energetically hydrolysed and eliminated as proteose. Doses of uranium nitrate which provoke only moderate symptoms

rapidly become fatal when Bence-Jones protein is also injected into the circulation, probably on account of the toxicity of the proteose formed from the injected protein.

After the death of the patient whose urine furnished the material for the above experiments, the urine taken from the bladder contained 3.6% of Bence-Jones protein, besides considerable albumin; the pleural fluid contained 0.11% and the blood about 0.2% of Bence-Jones protein. It is clear, therefore, that the protein circulates freely throughout the body. H. W. B.

Animal Diastases. I. The Increased Diastatic Activity of the Blood in Diabetes and Nephritis. VICTOR C. MYERS and JOHN A. KILLIAN (*J. Biol. Chem.*, 1917, **29**, 179—189).—The diastatic power is measured by incubating 2 c.c. of the oxalated blood with 1 c.c. of a 1% solution of soluble starch and 7 c.c. of water in a centrifuge tube for exactly fifteen minutes at 40°. About 1 gram of dry picric acid is added and the liquid centrifuged. The reducing power of 3 c.c. of the filtered supernatant fluid is then estimated by Myers and Bailey's method (*A.*, 1916, i, 300).

The results indicate that in cases of nephritis there is a two- to three-fold increase in the diastatic activity of the blood, which may possibly be explained by a decreased excretion of diastase in the urine. In diabetes, a still more pronounced increase in the diastatic power of the blood is noted. The bearings of this established fact on the current views of the etiology of diabetes are indicated, but the authors are unable at present to offer a satisfactory explanation of the cause of the condition. H. W. B.

Effects of Intravenous Injection of Arginine on the Creatine Content of Rabbits' Muscle. W. H. THOMPSON (*Proc. Physiol. Soc.*, ii—iii; *J. Physiol.*, 1917, **51**).—Arginine carbonate injected into rabbits in doses of 2—3 grams was transformed into creatine to the extent of 14.5% of the possible. The greatest increase in the muscle creatine observed was 0.0450%, which is brought about in six hours (under urethane anaesthesia). G. B.

Chemistry of Vegetable Physiology and Agriculture.

Vital Stains. WERNER SCHULEMANN (*Ber.*, 1917, **50**, 402—403). SIEGFRIED SKRAUP (*ibid.*, 641—645. Compare *A.*, 1916, i, 869).—Polemical. Mainly questions of priority. J. C. W.

Bacterial Decomposition of Polypeptides. ICHIRO OTSUKA (*Acta Scholae Med.*, Kyoto, 1916, **1**, 199—214; from *Physiol. Abstr.*, 1917, **2**, 15).—*Staphylococcus pyogenes aureus* and *Bacillus prodigiosus*, killed by toluene, resolve glycyl-L-tyrosine and glycyl-

tryptophan. Killed *B. coli*, on the other hand, which has no action on gelatin or blood serum, is also without effect on these dipeptides. The active cultures become inactive both as regards proteins and dipeptides, by filtration through a Chamberland filter. Comparison of proteolytic enzymes shows that trypsin remains active after filtration, but erepsin does not (compare Sasaki, this vol., i, 107). G. B.

Lactic Fermentation and Thallium Salts. Study on Heredity. CHARLES RICHET (*Ann. Inst. Pasteur*, 1917, 31, 51—59).—Amounts of thallium nitrate less than 0.001 gram per litre do not exercise any influence on the lactic ferment, but when the concentration reaches 0.0125 gram per litre the fermentation is diminished by 10% and with 0.125 gram per litre by 50%. If, however, the ferment is first accustomed to thallium nitrate by being grown on a medium containing 0.75 gram per litre, then in the presence of thallium nitrate to the extent of 0.125 gram per litre it produces a higher acidity than if the salt is absent. This toleration is not established immediately, but may require a period of eight days, but once established the bacillus produces a higher acidity than does a normal bacillus in the presence of the same thallium nitrate concentration. This toleration, while taking an appreciable time to establish, proceeds by a system of brusque mutations.

W. G.

The Formation of Starch by Moulds. FRIEDRICH BOAS (*Biochem. Zeitsch.*, 1917, 78, 308—312).—Moulds (*Aspergillus* and *Penicillium*) when grown on sugar solutions (5—10%) in the presence of ammonium salts (1—5%) at temperatures varying from 30° to 37° produce a substance giving the reactions of starch in the mycelia and also in the culture fluid. These results were obtained when dextrose, lævulose, and sucrose were employed, but not with lactose or maltose. The conclusion was drawn that the starch is formed in the presence of free mineral or organic acids (derived from the ammonium salts) under the influence of an enzyme.

S. B. S.

Rate of Turbidity in Beverages containing Maltose, Dextrose, or Maltose and Dextrose. A. W. HOMBERGER and C. S. MARVEL (*J. Amer. Chem. Soc.*, 1917, 39, 156—162).—Solutions containing either dextrose or maltose or equal weights of the two sugars and varying proportions of alcohol, carbon dioxide, and water were bottled under conditions which would prevent contamination from micro-organisms, and stored. Turbidity only occurred in those solutions which contained dextrose, the turbidity being due to the germination of the spores of *Penicillium glaucum*, the dextrose acting as a chemical stimulus. Maltose does not stimulate the spores of this mould, and hence maltose solutions do not grow turbid on keeping. The presence of alcohol and carbon dioxide has no appreciable effect on the appearance of the turbidity in dextrose solutions.

W. G.

Direct Estimations of Permeability. R. P. WODEHOUSE (*J. Biol. Chem.*, 1917, **29**, 453—458).—The author estimates the permeability of certain marine cells by comparing the composition of the sap inside the cell with that of the sea-water outside. The cells employed are those of the marine alga *Valonia*, individual cells of which are so large as to yield from 1 to 5 c.c. of sap.

The cell sap contains sodium, calcium, only a trace of magnesium, and an abundance of potassium; whilst the sea water contains sodium, calcium, magnesium, and only a relatively small quantity of potassium. The sap also differs from sea water in being free from sulphate. During life, therefore, the semipermeable protoplasmic membrane possesses a selective permeability which renders it impermeable to sulphates and yet permits of an accumulation of potassium ions within the cell. This selective permeability is lost at death; dead cells invariably contain sulphates, and if living cells are killed and replaced in sea-water, sulphate can soon be shown to be present inside.

H. W. B.

Exosmosis. S. C. BROOKS (*Amer. J. Botany*, 1916, **9**, 483—492).—The effect of salts on the permeability of the plasma membrane of cells was studied as follows. Strips of the peduncle of *Taraxacum officinale* Weber, were immersed in solutions of sodium chloride (0.22*M*), calcium chloride (0.16 or 0.17*M*), and cerium chloride (4.05*M*) for from fifteen to twenty minutes; they were then transferred to distilled water, and the rate of exosmosis was determined by the conductivity of the liquid. Sodium chloride increased the rate of exosmosis, calcium chloride decreased it, and cerium chloride first inhibited and then accelerated exosmosis. It was found possible to make up a balanced solution which left the permeability of the protoplasm unaltered. This consisted of 80 parts of sea-water to 20 parts of 0.52*M* calcium chloride solution, the whole diluted to 21/52 of the original concentration.

L. M. U.

A Study of Permeability by the Method of Tissue Tension. S. C. BROOKS (*Amer. J. Botany*, 1916, **10**, 562—570).—Strips of *Taraxacum officinale* Weber, when cut, curl outwards owing to the tension of the cells. If placed in slightly hypertonic solutions, their curvature first decreases and then increases until it exceeds the original curvature, indicating that the recovery of the plasmolysed cells has occurred. This phenomenon was taken as the basis of a method for determining the permeability of cells. The strips of tissue were placed in a slightly hypertonic solution, and the time of recovery was noted; then the concentration of the solution was gradually increased by the addition of measured amounts of a strong solution, and with each addition the time of recovery was observed again. Finally, the rate of penetration was expressed empirically by dividing the time of recovery by the increase in concentration of the solution. Assuming that the permeability remained normal in a balanced solution of sea-water and calcium chloride (see previous abstract), then salts of univalent cations

(sodium, potassium, ammonium) caused a rapid increase in permeability, whilst salts of bi- and ter-valent cations (calcium, magnesium, cerium, aluminium) caused a very great decrease in permeability. Sucrose penetrated the protoplasm quite rapidly and affected permeability like the univalent cations. L. M. U.

The Physiological Significance of Potassium in Plants. TH. WEEVERS (*Biochem. Zeitsch.*, 1917, **78**, 354—357).—According to the author, potassium salts play an important part in the formation of the proteins of plants. This conclusion is not in accordance with that arrived at by Stoklasa (A., 1916, i, 354). The results of this author are criticised, and it is claimed that his experiments were not carried out in the complete absence of potassium, and furthermore, that if his results as to the amount of protein are stated in absolute amounts instead of in percentages (on the dwarf plants produced when they are grown without potassium) the experiments do not indicate any production of protein. S. B. S.

Occurrence of Free Carbon Monoxide in Kelp (*Nereocystis luetkeana*). SETH C. LANGDON (*J. Amer. Chem. Soc.*, 1917, **39**, 149—156. Compare Zeller and Neikirk, *Puget Sound Marine Stat. Pub.*, 1915, **1**, 25—30).—An examination of the gas contained in the floaters of the large Pacific coast kelp, *Nereocystis luetkeana*, does not confirm the results of Zeller and Neikirk (*loc. cit.*) as to the presence of appreciable quantities of carbon dioxide and the variation of the carbon dioxide and oxygen content with the time of day. The author now shows that the gas present in the floater contains carbon monoxide, the quantity varying considerably in different individual specimens over a range of from 0.2 to 12.4%, averaging 4%. The oxygen content was also higher than that found by Zeller and Neikirk, averaging 18%. The gas in the floater is under diminished pressure, the pressure readings being very irregular. At present there is no definite indication that the composition of the gas in the floater varies with the time of the day, that is, with the light intensity. The highest carbon monoxide content is to be found in the larger and more healthy kelps which grow where the tidal currents are swiftest. W. G.

Evidence of the Action of Oxydases within the Growing Plant. JOSEPH H. KASTLE and G. DAVIS BUCKNER (*J. Amer. Chem. Soc.*, 1917, **39**, 478—482).—A solution of phenolphthalin was injected into the centre of the stalk of sweet corn plants 6—7 ft. high at various distances below the tassel. The stalk was then cut off 8 in. below the point of injection, and cross-sections at once made at different intervals along the stalk. It was found on examination that the reagent had been completely oxidised to phenolphthalein. Similar results were obtained with a young stalk cut off just above the roots and the cut end inserted into a freshly prepared solution of phenolphthalin. Similar results were also

obtained with injection experiments with the okra plant. Oxidation must apparently, therefore, go on in the living cell. W. G.

Specific Action of Barium. W. J. V. OSTERHOUT (*Amer. J. Botany*, 1916, 9, 481—482).—On placing certain species of *Spirogyra* in 0·0001*M*-barium chloride, a peculiar and very characteristic contraction of the chloroplasts was obtained. In the neighbourhood of the nucleus, the chloroplasts contracted so strongly that they formed a very compact, green mass like a twisted rope, the diameter of this mass being one-fourth to one-third of that of the cell. At the ends, little or no contraction occurred, and in no part of the cell did the protoplasm contract away from the cell wall, showing that this process is different from false plasmolysis, which may occur later if the exposure is sufficiently prolonged. Strontium chloride produced the same effect at higher concentrations (0·001*M* and higher), but the chlorides of calcium, magnesium, manganese, cadmium, nickel, cobalt, sodium, potassium, and ammonium did not at any concentration. L. M. U.

Copper in the Flora of a Copper-tailing Region. W. G. BATEMAN and LANSING S. WELLS (*J. Amer. Chem. Soc.*, 1917, 39, 811—819).—An examination of the effects caused by the tailings of a large copper smelter on the native flora of the district. Most of the flora of the district seemed to have been destroyed, among the larger shrubs only the wild rose appearing to flourish. The plants grown in the region were found to contain appreciable amounts of copper, arsenic, antimony, and tin, the amounts of copper ranging from 0·0046% to 0·621%, being higher in the dead than in living tissues and greater in the bark than in other parts of the plant. W. G.

The White Turbidity of Wines. FONZES-DIACON (*Compt. rend.*, 1917, 164, 199—200).—The examination of the precipitate formed in a white wine by atmospheric oxidation shows it to contain some organic matter in addition to mineral matter. The latter portion contains a very small amount of calcium, together with a larger amount of iron, which is combined with phosphoric acid in the proportion corresponding with basic ferric phosphate, $\text{Fe}_2\text{O}_3(\text{P}_2\text{O}_5)_2$. The precipitate is only obtained when the sulphurous acid, present in all white wines, is oxidised, and the presence of a trace of calcium, together with an excess of iron and phosphoric acid, are indispensable for its formation. The use of sulphurous acid solutions of ammonium phosphate in place of potassium metabisulphite in vinification appears to be one of the most important causes of this precipitation. W. G.

The Reactions of the White Turbidity of Wines. J. LABORDE (*Compt. rend.*, 1917, 164, 441—443. Compare A., 1904, ii, 278).—A claim for priority over Fonzes-Diacon (preceding abstract). W. G.

The Turbidity of Wines. FONZES-DIACON (*Compt. rend.*, 1917, 164, 650—652. Compare preceding abstracts).—The author admits the priority of Laborde, and points out that the modern process of vinification by sulphurous solutions of ammonium phosphate predisposes wines, and particularly white wines, to this turbidity ("casé"). It can be lessened or prevented by the addition of citric acid, but the legal amount is sometimes insufficient.

W. G.

The Phytic Acid of the Wheat Kernel and some of its Salts. P. W. BOUTWELL (*J. Amer. Chem. Soc.*, 1917, 39, 491—503).—Phytin was extracted from wheat bran and the wheat embryo by a modification of the method used by Clark with Indian field mustard seed (compare T., 1914, 105, 535). The phytin, so prepared, was free from inorganic phosphates and was shown to be a crystalline calcium-magnesium salt, insoluble in water. In composition it does not agree with any of the simple calcium-magnesium salts of inositol-hexaphosphoric acid. The carbon and phosphorus are present, however, as in phytic acid, in equal numbers of atoms. Free phytic acid was prepared from this phytin, and differed from the phytic acid previously described in that it was an amber-coloured solid, undergoing spontaneous decomposition while drying in a vacuum. Crystalline barium salts were obtained from the crude phytin, the salt crystallised from cold dilute hydrochloric acid having the composition $C_6H_{12}O_{24}P_6Ba_3 \cdot C_6H_{10}O_{24}P_6Ba_4 \cdot 14H_2O$, and that crystallised from boiling dilute hydrochloric acid having the composition $2(C_6H_{12}O_{24}P_6Ba_3) \cdot C_6H_{10}O_{18}P_4Ba_3 \cdot 15H_2O$. Phytin thus seems to exist in the wheat kernel as salts of inositol-phosphoric acid, phytic acid being an ester of inositol and phosphoric acid.

The second part of the paper deals with the activity of the phytase of wheat bran and embryo under different conditions (compare Anderson, A., 1915, i, 634). In 0.2% hydrochloric acid the activity of the phytase as indicated by the production of inorganic phosphoric acid is inhibited, being only about one-third of its activity in 0.1% hydrochloric acid, which is the optimum acidity. Dry heat increases the amount of inorganic phosphorus extracted from wheat-bran, without apparently destroying the enzyme. The activity of phytase is not affected by formaldehyde.

W. G.

Assimilation of Organic Nitrogen by Zea mais and the Influence of Bacillus subtilis on such Assimilation. REED O. BRIGHAM (*Soil Sci.*, 1917, 3, 155—195).—In the first part of the paper a historical survey of the work on this subject is given.

Two varieties of corn, namely, *Zea mais everta* (pop corn) and *Zea mais indentata* (dent corn), were grown on sterile 1% agar containing the necessary plant nutrients except nitrogen, this being added in the form of various organic substances and the effect on the plant growth observed either in the presence or absence of *B. subtilis*. The seeds were first sterilised, germinated on moist filter-paper in sterile petri dishes, and then the seedlings trans-

ferred to the agar. Units showing signs of infection were rejected.

Zea mais directly assimilates and uses the organic nitrogen supplied in the form of asparagine, casein, cotton-seed meal, haemoglobin, linseed meal, uric acid, peptone, guanine, alanine, urea, creatine, malt, and glycine, named in the order of their availability. Guanidine carbonate and nitrate, dip' enylamine, caffeine, and benzamide are toxic to *Zea mais*. Guanir' is toxic to pop corn, but not to dent corn. Compounds containing a benzene nucleus were found to be exceedingly toxic to the plants tried. In the case of dent corn the six substances named first above were more effective than sodium nitrate in promoting growth, and ammonium sulphate is a far better source of nitrogen than sodium nitrate for this plant. The two varieties of *Zea mais* reacted differently with some of the nutrient substances.

In the presence of *B. subtilis* eight of the organic substances which were directly available produced better growth, probably because of ammonification. Generally speaking, those organic compounds of high complexity in composition are better after ammonification, whilst those of a low degree of complexity are not improved by ammonification.

The author considers that the method of determining growth by measuring the total length of the leaves gives results very nearly parallel to those obtained by determining the dry weights of the plant and is much simpler and quicker. W. G.

Non-specificity of the Animal and Vegetable Reducing Ferment. A. BACH (*Compt. rend.*, 1917, 164, 248—249).—An examination of the reducing action of the ferment present in milk or potato pulp (compare A., 1916, i, 682) on nitrates in the presence of a number of aldehydes shows that it is independent of the complex to which the aldehyde group is attached. The specificity of the ferment is functional and not structural. Certain aldehydes are better utilised by the vegetable than by the animal ferment.

W. G.

Hydrolysis of the Soluble Protein of Swede Turnips. GWILYM WILLIAMS (*J. Agri. Sci.*, 1917, 8, 182—215).—The author has prepared a quantity of the soluble protein from the expressed juice of swede turnips by precipitation, the juice being heated at 90° for half an hour. The protein thus prepared contained N=14.09%; H₂O=1.81%; ash, 8.60%; S=4.204%. The value for the sulphur is particularly high, much of it probably coming from the ash. The protein was hydrolysed and the amounts of the various amino-acids present determined, the following results being obtained, expressed as percentages of the dry ash-free protein: Glycine, 0.27%; alanine, 3.58%; valine, 9.95%; leucine and iso-leucine, 9.01%; phenylalanine, 4.47%; tyrosine, 2.92%; cystine present; proline, 4.17%; aspartic acid, 6.98%; glutamic acid, 3.18%; tryptophan present; arginine, 3.12%; histidine, 3.04%; lysine, 4.35%; ammonia, 1.21%; humin substances, 4.74%; total, 60.99%. The protein shows no excessive content of any particular amino-acid

and all the usual "Bausteine" are present. The glutamic acid content is low as compared with other vegetable proteins and the valine content unusually high.

W. G.

The Organic Matter of the Soil. IV. Some Data on Humus-phosphoric Acid. ROSS AIKEN GORTNER and WILLIAM M. SHAW (*Soil Sci.*, 1917, 3, 99—111. Compare this vol., i, 248, 310, 311).—Estimations have been made of the phosphoric acid content of the ammonia extracts of eight soil types, peats, and unchanged vegetable materials, before and after leaching with 1% hydrochloric acid, and also of the amount extracted by this acid. Four per cent. ammonium hydroxide extracted more phosphoric acid from the air-dry soil in seven of the eight soil types than did the 1% hydrochloric acid. There is no apparent relation between the amounts of phosphoric acid extracted by the ammonium hydroxide before and after the soil was leached with 1% hydrochloric acid. The greater part of the phosphoric acid present in humus ash is probably inorganic, being derived from colloidal clay and from adsorption by the colloids present. There is no apparent relationship between the total nitrogen in the soil and the phosphoric acid extracted by the different treatments. The phosphoric acid present in the ammonia extract of soils cannot be correlated either with the organic matter present or with the known fertility of the soil type. The humification of vegetable materials in contact with a soil for a year did not increase the humus-phosphoric acid over that contained in the original subsoil.

W. G.

α -Crotonic Acid, a Constituent of the Soil. E. H. WALTERS and LOUIS E. WISE (*Journ. of Agric. Res.*, 1916, 6, 1043—1045; from *Chem. Zentr.*, 1916, i, 121—122).—The authors have isolated α -crotonic acid, m. p. 72°, from a barren, fine sandy loam from Texas, which formed a layer eight to eighteen inches thick over impervious clay. The soil was poor in lime and other bases, very faintly dehydrated, and had a high reducing and only very low oxidising action. For the isolation of the acid, the soil was treated for twenty-four hours with sodium hydroxide solution (2%) at the ordinary temperature; the extract was faintly acidified with sulphuric acid and extracted with ether. The ethereal solution was shaken with sodium hydrogen sulphite to remove aldehydes and other substances, and the sulphite solution repeatedly agitated with fresh ether. α -Crotonic acid was isolated from the brown, syrupy residue obtained by evaporating the ethereal extracts, 94 mg. of acid being obtained from 22.5 kilos. of soil. Owing to experimental losses, this figure must be regarded as a minimum value. The acid may possibly be formed from the β -hydroxy-acids obtained by the decomposition of cellulose or from allyl cyanide which is present in the ethereal oils of certain plants.

H. W.

Organic Chemistry.

The Aliphatic Terpenes. C. J. ENKLAAR (*Rec. trav. chim.*, 1917, **36**, 363—365. Compare this vol., i, 111).—Polemical. A reply to Auwers and Eisenlohr (compare A., 1911, ii, 782).

W. G.

Preparation of Nitromethane and Homologues. H. KRAUSE (D.R.-P., 294755; from *J. Soc. Chem. Ind.*, 1917, **36**, 520).—An intimate mixture of a nitrite and a salt of an alkyl hydrogen sulphate is made into a cream with water and distilled. Above 100° the nitroparaffin passes over, and this continues after the mass has been evaporated to dryness. Decomposition of the alkyl sulphate to form sulphuric acid or an acid sulphate is to be avoided, since it causes a loss of yield which is further augmented because the free sulphuric acid liberates nitrous acid, which then reacts with the nitroparaffin. To obviate this, a little alkali, or a salt with an alkaline reaction, is added to the mixture previous to distillation. The yield of nitromethane is 50%, of nitroethane 35%, of that theoretically possible.

H. W.

Preparation of Glycols. GULF REFINING CO. (U.S. Pat., 1215903; from *J. Soc. Chem. Ind.*, 1917, **36**, 472).—Glycols are obtained by heating dichloro-olefines under pressure with an alkali formate and an alcohol, for example, methyl alcohol. The temperature may vary between 140° and 200° and the pressure from 7 to 18 kilos. per sq. cm.

H. W.

Preparation of Acetic Acid from Acetaldehyde. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P., 294724; from *J. Soc. Chem. Ind.*, 1917, **36**, 503).—Acetaldehyde is oxidised by air or oxygen in presence of iron compounds and organic salts of alkalis or alkaline earths, including magnesium and aluminium. The reaction is accelerated without the formation of per-acids. It proceeds rapidly and completely in the cold.

H. W.

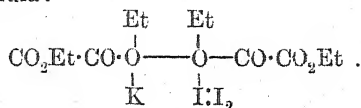
Hydrogenisation and Dehydrogenisation of Carbon Compounds. BADISCHE ANILIN- & SODA-FABRIK. (U.S. Pats. (A), 1215334, (B) 1215335; from *J. Soc. Chem. Ind.*, 1917, **36**, 473. Compare A., 1915, i, 765).—Specific claim is made for the use, as catalysts, of mixtures of (A) nickel and boron oxide, and (B) nickel and calcium phosphate.

H. W.

Complex Organic Manganese Compounds. II. P. E. VERKADE (*Chem. Weekblad*, 1917, **14**, 420—425. Compare *ibid.*, 34).— α -Hydroxy-acids, as well as pyruvic acid, malonic acid, and certain of their alkyl derivatives, react with hydrated manganese dioxide to form brown solutions, which are rapidly decomposed by heat, with formation of carbon dioxide, an aldehyde or ketone with

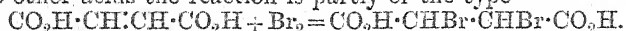
one carbon atom less than the parent acid, and the manganese salt of the acid. Aromatic hydroxy-acids form similar coloured solutions, but these are not decomposed by heat. A. J. W.

A Compound of Ethyl Oxalate with Potassium Tri-iodide. A. SKRABAL (*Ber.*, 1917, **50**, 581—582).—When a fresh solution of ethyl oxalate is mixed with iodine dissolved in potassium iodide, large, lustrous, polychroic (golden to dark blue) crystals are gradually deposited. The compound is apparently an oxonium periodide of the formula:



J. C. W.

The Formation and Decomposition of some Organic Halogenated Compounds. EINAR BILMANN (*Rec. trav. chim.*, 1917, **36**, 313—328).—A quantitative study of the action of bromine water on certain unsaturated acids. The acids examined were fumaric, maleic, mesaconic, itaconic, acrylic, and crotonic acids. The results show that the bromine enters these acids principally in the form of hypobromous acid, $\text{CO}_2\text{H}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H} + \text{Br}_2 + \text{H}_2\text{O} = \text{CO}_2\text{H}\cdot\text{CHBr}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H} + \text{HBr}$. In the case of fumaric and crotonic acids this is almost the total reaction, but with some of the other acids the reaction is partly of the type



In the presence of a large excess of potassium bromide, there is a greater tendency for the second reaction to occur.

By measuring the initial velocities in solutions of very varied concentrations, the action of potassium iodide on $\alpha\beta$ -dibromopropionic acid in the presence of sulphuric acid is shown to be bimolecular and to follow the course $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CO}_2\text{H} + 3\text{KI} = \text{CH}_2:\text{CH}\cdot\text{CO}_2\text{H} + 2\text{KBr} + \text{KI}_3$. The reaction is not reversible to any appreciable extent. W. G.

Rotatory Powers of Tartrates of Substituted Amines. LUIGI CASALE (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 434—438; *Gazzetta*, 1917, **47**, i, 191—196).—The author has measured the rotatory powers of a number of tartrates and hydrogen tartrates of the alkali metals and of a number of aromatic and aliphatic amines. From the numerical results obtained, the following conclusions are drawn.

In dilute aqueous solution and at the ordinary temperature the hydrogen tartrates of organic bases exhibit molecular rotations identical with those found for the hydrogen tartrates of the alkali metals, and are, therefore, not hydrolysed. Under the above conditions, the normal tartrates of aliphatic amines also possess molecular rotatory powers equal to those given by the corresponding alkali salts, and thus do not undergo hydrolytic dissociation. Under the same conditions, the normal tartrates of aromatic amines exhibit

molecular rotations which are markedly inferior to those shown by the corresponding salts of the aliphatic amines and increase with increase in the concentration of the base in solution; they are, therefore, partly hydrolysed.

These results disprove: (1) Kannonikov's statement, based on the equality of the specific rotations of normal tartrates of the weak bases to that of tartaric acid, that these tartrates undergo complete hydrolytic dissociation (A., 1892, 1308), and (2) Minguin and Wohlgenuth's conclusion that the acid salt formed by the combination of one molecule of tartaric acid with one molecule of an aromatic amine is very appreciably hydrolysed, and that the addition of further proportions of the base diminishes and finally annuls the hydrolysis (A., 1909, i, 11). T. H. P.

Pectin Substances. II. Algic and Fucic Acids. SVEN ODÉN (*Int. Zeitsch. phys.-chem. Biol.*, 1917, 3, 83—93. Compare this vol., i, 436).—The electrical conductivities of suspensions of algic and fucic acids (Kylin, A., 1915, i, 931) treated with dilute ammonium hydroxide undergo similar changes to those previously described (*loc. cit.*). Both substances are therefore true acids, forming soluble salts on treatment with alkalis. When gelatin is similarly tested, it is found to have very slight acidic properties, which may be due to impurities.

Fucic acid has the empirical formula $C_{10}H_{18}O_{11}$, mol. wt. 160, and properties which lead the author to suggest that the substance is a dipentenedicarboxylic acid, $O(C_4H_5O_3 \cdot CO_2H)_2$. H. W. B.

Crystallisation and Properties of a β -Monoglucoside of Glycerol previously obtained by Biochemical Synthesis. EM. BOURQUELOT, M. BRIDEL, and A. AUBRY (*Compt. rend.*, 1917, 164, 831—833. Compare A., 1915, i, 703).—The glucoside prepared by the action of emulsin on a solution of glycerol and dextrose has now been obtained in a crystalline form from its alcohol-ether solution on long keeping. It crystallises in elongated prisms, m. p. 130—135°; $[\alpha]_D -28^\circ 16'$, and does not reduce Fehling's solution. W. G.

Preparation of β -Ethyl Galactoside by means of the Kernels of Apricots, Peaches, and Cherries, the Seeds of Apples, and Bitter-almond Cake. MOUGNE (*J. Pharm. Chim.*, 1917, [vii], 15, 345—348).—Using the β -galactosidase preparation obtained from the above sources (compare this vol., i, 438), the author has, in all cases, been able to synthesise β -ethyl galactoside from galactose and ethyl alcohol. W. G.

The Biochemical Synthesis of Alkyl Glucosides. IV. Alkyl Galactosides. EM. BOURQUELOT (*Ann. Chim.*, 1917, [ix], 7, 153—226).—A résumé of work already published (compare A. 1912, i, 946; 1913, i, 249, 498, 1045; 1914, i, 1125; 1915, i, 382, 501; 1916, i, 413, 596, 711, 792). W. G.

New Hydrazones of some Monosaccharides (*p*-Tolylhydrazones of *l*-Arabinose, Rhamnose, Fucose, *d*-Mannose, and *d*-Galactose). A. W. VAN DER HAAR (*Rec. trav. chim.*, 1917, 36, 346—351).—The following *p*-tolylhydrazones were prepared by warming the sugar and *p*-tolylhydrazine together in alcoholic solution. They are best crystallised from alcohol. *l*-Arabinose-*p*-tolylhydrazone, colourless, prismatic needles, m. p. 160°; *rhamnose-p*-tolylhydrazone, colourless leaflets, m. p. 166°; *d*-mannose-*p*-tolylhydrazone, colourless, rhomboidal plates, m. p. 190—191°; *fucose-p*-tolylhydrazone, long, colourless needles, m. p. 169°; *d*-galactose-*p*-tolylhydrazone, colourless, prismatic batons, m. p. 168°. Microphotographs of the crystals are given in the original. These *p*-tolylhydrazones are less soluble than the corresponding phenylhydrazones. Crystalline *p*-tolylhydrazones could not be obtained from xylose, *d*-fructose, or dextrose. W. G.

Product of Deflagration of Cellulose Nitrate. ELIGIO TRAPANI (*Atti R. Accad. Lincei*, 1917, [v], 26, i, 332—334).—If a small quantity of a smokeless nitrocellulose powder, such as ballistite, cordite, or one based on cellulose nitrate alone, is carefully heated until it deflagrates, a pungent odour resembling that of formaldehyde is observable. Further, if the cold residue is treated with water and with sodium carbonate to neutralise the nitrous acid formed, the liquid obtained gives with phenylhydrazine hydrochloride and sodium nitroprusside the blue coloration characteristic of the presence of formaldehyde. The formaldehyde may be derived from the residue, $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, possibly existing in the cellulose nitrate or from some analogous chain formed in an early stage of the decomposition as a result of processes of denitration. Hydroxypyruvic acid constitutes one of the thermal decomposition products of cellulose nitrate, and this may yield formaldehyde by further degradation. The presence of formaldehyde is also probably related to that of carbon monoxide and hydrogen, which are formed on explosion of cellulose nitrate. T. H. P.

Aliphatic Hydroxylammonium Salts and Hydroxamic Acids with Halogen Substituents. LAUDER WILLIAM JONES and LOUIS F. WERNER (*J. Amer. Chem. Soc.*, 1917, 39, 413—422).—When chloro-, dichloro-, or trichloro-acetic acid is gradually added in the molten state to the calculated quantity of hydroxylamine at 0° and the mixture thoroughly stirred, the corresponding hydroxylammonium salt is obtained. *Hydroxylammonium chloroacetate* has m. p. 124—125°; the *dichloroacetate*, m. p. 116—116.5° (decomp.); and the *trichloroacetate*, m. p. 133—134°. When these chloroacetates are heated to their melting points variable amounts of the corresponding hydroxamic acids are formed, but owing to their instability at these temperatures the method is impracticable for preparing these hydroxamic acids. With bromo- and iodoacetic acids the halogens are so readily replaceable that the hydroxylammonium salts of these acids could not be obtained in the pure state.

Chloroacethydroxamic acid, m. p. 92—93°, is readily obtained by the addition of hydroxylamine to an alcoholic solution of ethyl chloroacetate. It gives an *acetyl* derivative, m. p. 85—86°; a white *sodium* salt, which when heated explodes with a yellow flame; a white *silver* salt, which soon decomposes, giving metallic silver; and a green *basic copper* salt, $C_4H_6O_5N_2Cl_2Cu_2$. The free acid when kept for four days is spontaneously converted into an *isomeride*, m. p. 108—108·5°, which gives an *acetyl* derivative, m. p. 67°.

When ethyl bromoacetate is added to a cold alcoholic solution of hydroxylamine, in a few minutes "basic" hydroxylammonium bromide, $[NH_2(OH)]_2HBr$, m. p. 110°, separates. A hydroxamic acid is also formed, but cannot be isolated. If the "basic" hydroxylammonium bromide is not removed, a further reaction occurs, and a compound, $C_8H_{15}O_5N$, m. p. 65°, is obtained, which the authors consider is a $\beta\beta$ -disubstituted hydroxylamine, $HO\cdot N(CH_2\cdot CO_2Et)_2$. A similar reaction occurs with hydroxylamine and ethyl iodoacetate, the same compound, m. p. 65°, being obtained.

Bromoacethydroxamic acid, m. p. 103°, was finally prepared by mixing bromoacetyl bromide with hydroxylammonium chloride in aqueous solution containing sodium carbonate. The acid was separated as its green *basic copper* salt. *Iodoacethydroxamic acid*, m. p. 107·5° (corr.), was similarly prepared from iodoacetyl chloride and gave a dark green, normal *copper* salt. W. G.

Isomerism of the Polypeptides. EMIL FISCHER (*Zeitsch. physiol. Chem.*, 1917, **99**, 54—66).—The author gives formulæ for calculating the number of possible isomeric polypeptides containing amino-acids, of which some are alike and others different. The effects of the introduction of the diamino-acids and of cystine are taken into account, and, in simple cases, the influence of optical isomerism is dealt with. Fischer's octadecapeptide (A., 1907, i, 485), for instance, has 816 possible isomerides, whilst a complex polypeptide or protein containing 30 amino-acids, of which 5 are glycine, 4 alanine, 3 leucine, 3 lysine, 2 tyrosine, 2 phenylalanine, and the remaining 13 are other amino-acids, has no fewer than $1\cdot28 \times 10^{27}$ possible isomerides. The latter calculation is based on the assumption that the amino-acids are combined only in the simplest possible way, such as occurs between mono-aminomonocarboxylic acids. H. W. B.

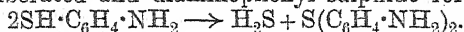
The Nitrogenous Pigments of Molasses. VL. STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1917, **41**, 298—306).—When dried molasses is extracted with alcohol, there remains undissolved a small percentage of non-saccharine substances which contain about 94% of the total pigment and 10% of the nitrogen of molasses. The question whether any of the nitrogen is present in a highly coloured compound naturally presents itself, and so the author has separated the residue into various fractions. One of them apparently contains a fairly definite substance which is precipitated by lead

acetate, is soluble in alcoholic hydrogen chloride solution, but not in ether, and contains 7.1—7.3% of nitrogen and about 0.2—0.3% of ash. It seems to be a product of the condensation of amino-acids with sugars, and is designated *fuscazinic acid*. The alkali salts of this account for about half of the colour of molasses.

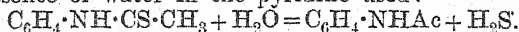
J. C. W.

Action of Pyridine and of Piperidine on certain Organic Sulphur Compounds. III. M. RAFFO and O. BALDUZZI (*Gazzetta*, 1917, 47, i, 65—73. Compare A., 1915, i, 86).—Just as when treated with mercuric oxide, thiocarbamide also loses sulphur when its pyridine solution is boiled, but in this case the final product is guanidine thiocyanate, which undergoes change with extreme readiness and could not be analysed; hydrogen sulphide is also formed, together with a compound regarded as ammonium trithiocarbonate.

When a pyridine solution of thioaminophenol is boiled, hydrogen sulphide is liberated and diaminophenyl sulphide formed:



Under similar treatment, thioacetanilide yields hydrogen sulphide and acetanilide, the formation of the latter being apparently due to the presence of water in the pyridine used:

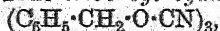


The desulphurising action of pyridine is not exclusive to this base. When a solution of diphenylthiocarbamide in piperidine is boiled in a reflux apparatus, hydrogen sulphide is evolved, and unstable, white needles, which apparently consist of piperidine hydrosulphide, form in the condenser; if the boiling is continued, the final products obtained are aniline, triphenylguanidine, and the piperidine derivative, $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CS}\cdot\text{SH}$, $\text{C}_5\text{H}_{11}\text{N}$. T. H. P.

Investigations in the Cyanic Acid Series. EINAR BILLMANN and JOHANNE BJERRUM (*Ber.*, 1917, 50, 503—510).—The molecular complexity of cyanurates in the gaseous state, the isomerism of cyanurates and *isocyanurates*, and the action of phosphoric oxide on urethanes are discussed.

Trimethyl cyanurate is termolecular in the state of vapour, as measured by Victor Meyer's method in a bath of boiling benzophenone. At the boiling point of sulphur it suffers partial decomposition, but even so the volume of vapour does not indicate that much depolymerisation has taken place.

When silver cyanurate is treated with alkyl iodides in excess, *isocyanurates* are formed as well as cyanurates. Some light is thrown on this reaction by the fact that in certain cases it has been possible to convert a cyanurate into an *isocyanurate* by heating it with an alkyl haloid. It appears that the alkyl haloid is attached to the nitrogen atoms, and that the alkyl radicles already linked to oxygen are then ejected in combination with the halogen atoms. Thus, trimethyl cyanurate yields the *isocyanurate* when heated with methyl iodide, and tribenzyl *isocyanurate* when boiled with benzyl bromide. True *tribenzyl cyanurate*,



m. p. 102—103° (from sodium benzyloxide and cyanuric chloride), also yields the *isocyanurate* when heated with benzyl bromide.

When carbamates are heated with phosphoric oxide, they might be expected to yield cyanates, thus: $\text{RO}\cdot\text{CO}\cdot\text{NH}_2 \rightarrow \text{RO}\cdot\text{CN}$. They give allophanates, however, according to the scheme: $2\text{RO}\cdot\text{CO}\cdot\text{NH}_2 = \text{RO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 + \text{R}\cdot\text{OH}$, ethyl and methyl allophanates being most readily obtained from the corresponding carbamates. Xanthamide yields a small quantity of ethyl dithio-allophanate, thus: $\text{OEt}\cdot\text{CS}\cdot\text{NH}_2 \rightarrow \text{OEt}\cdot\text{CS}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$, but also suffers rearrangement into ethyl thiourethane, and so gives ethyl thiocyanate as well, thus: $\text{SEt}\cdot\text{CO}\cdot\text{NH}_2 \rightarrow \text{SEt}\cdot\text{CN}$.

In the hope of transforming ethyl nitrite into nitroethane by means of ethyl iodide, so as to give a similar explanation to the production of these isomerides by the action of ethyl iodide on silver nitrite, the reagents were heated in a sealed tube, but a violent explosion occurred when the cold tube was opened.

J. C. W.

New Fulminates and Azides. LOTHAR WÖHLER and F. MARTIN (*Ber.*, 1917, 50, 586—596).—Some new fulminates have been obtained by the interaction of mercury or silver fulminate and the amalgam of the particular metal in dry methyl alcohol, the salt being precipitated from the solution by means of ether, and all the operations being conducted in an atmosphere of hydrogen.

Cadmium fulminate, $\text{Cd}(\text{CNO})_2$, is a white powder which is quite stable when dry, but readily decomposed by water, in which it is very soluble. It retains about 1% of methyl alcohol tenaciously. It is one of the most violent explosives, and is nearly as sensitive to shock and heat as mercury fulminate. *Thallous fulminate* becomes superficially yellow in the light, and is very sensitive to moisture. It is the most susceptible of all known fulminates to shock and increased temperature, but the heat of detonation is not high, and so its explosion is not so violent. *Cuprous fulminate* is insoluble in water, and so may be prepared in aqueous media. It is pale grey (probably white; compare cuprous chloride) and is almost as violently explosive as cadmium fulminate, although not so sensitive to shock.

The preparation of mercury fulminate, and of the amalgams required for the above experiments, and the analysis of the salts are described. Details as to the value of these fulminates in explosives technology are being published elsewhere.

Some new azides have also been prepared, by shaking together finely divided, dry metallic carbonates or basic azides with an ethereal solution of azoimide until a portion of the solid is found to be completely soluble in water. *Nickel azide* is a sandy, green powder which absorbs water and holds it (about 13%) tenaciously; it is very soluble in water, but soon suffers hydrolysis. It is very sensitive to pressure, even gentle rubbing causing a most violent explosion. *Cobalt azide* is still more explosive, and is even more

dangerous than lead or silver azides. The ethereal liquid left from the preparation is reddish-brown and apparently contains a complex cobaltihydrazoic acid, for silver nitrate gives a brown precipitate instead of white silver azide. *Zinc azide* is a white, sandy powder which is very hygroscopic, and therefore usually obtained with associated water. It is readily hydrolysed, but is no more explosive than the alkaline earth azides. *Manganous azide* can only be obtained from the known basic azide. It is also white, hygroscopic, and easily hydrolysed, and explodes more violently than the zinc salt, but less so than the cobalt salt. *Ferric azide* has been obtained in very dark brown, hygroscopic leaflets by evaporating the solution formed when dry ferric sulphate and sodium azide are shaken with dry methyl alcohol. The well-known deep red colour of the solution of ferric azide, the formation of sodium azide by the action of nitrous oxide on sodamide, and of sodium thiocyanate by the action of carbon disulphide on sodamide, and the explosive nature of fulminates and azides, are commented on, in support of Thiele's formula for azoimide, the acids being represented thus: HN:N:N , $\text{HS}\cdot\text{C:N}$, $\text{HO}\cdot\text{N:C}$. Chromium hydroxide gives a very dark green, hygroscopic *complex*, probably of the formula $[\text{Cr}(\text{N}_3)_3\text{OH}]\text{H}$.

The heats of detonation in calories per gram of the fulminates and azides are given in the following table:

	Azides.	Fulminates.
Ag	452	470
Pb	364	—
Cu'	532	508
Hg'	266	—
Cd ..	553	470
Tl'	232	223
Ni	656	—
Zn	360	—
Mn''	676	—
Ca	625	—
Sr	295	—

J. C. W.

Organo-lead Compounds. VII. Lead Tetra-alkyls with Secondary Alkyl Radicles, and their Behaviour towards Halogens. GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1917, 50, 574—580. Compare A., 1916, i, 684, 799, 800; this vol., i, 256, 257).—Lead tetra-alkyls containing one or two secondary alkyl radicles can be obtained quite readily by the action of the magnesium *sec.*-alkyl haloids on lead alkyl mono- or di-haloids. The attachment of lead to a secondary carbon atom is much weaker than to a primary, and therefore the new compounds differ in important respects from the many lead tetra-alkyls with normal radicles which have already been described. In the first place they are not stable in the air, but soon deposit flocculent products. Then the secondary radicle is expelled by bromine at -75° with great ease, even before a lighter normal group. If two such groups are present, both are expelled, whereas in the case of

normal alkyl radicles only one is removed at this temperature. *Lead tetraisopropyl*, obtained by the action of magnesium isopropyl chloride on lead chloride, has m. p. -53.5° (corr.), b. p. $120^{\circ}/14$ mm., D_4^{25} 1.4578, n_{H_a} 1.52102, n_D 1.52600, n_{H_s} 1.53938, n_{H_v} 1.5110, at 12° . *Lead trimethylisopropyl* has b. p. $75^{\circ}/60$ mm., D_4^{25} 1.7403, n_{H_a} 1.5042, n_D 1.5095, n_{H_s} 1.5223, n_{H_v} 1.5335, at 20° . *Lead dimethylethylisopropyl* has b. p. $61.2^{\circ}/15$ mm., D_4^{25} 1.6968, n_{H_a} 1.50812, n_D 1.51327, n_{H_s} 1.52614, n_{H_v} 1.53731, $n_F - n_C$ 0.01801, at 20.6° . *Lead dimethylethyl-sec.-butyl*, $PbMe_2Et \cdot CHMeEt$, has b. p. $75^{\circ}/14$ mm., D_4^{25} 1.6322, n_D^{21} 1.5140, $n_F - n_C$ 0.01711. *Lead dimethylethyl-sec.-amyl*, $PbMe_2Et \cdot CHMePr$, has b. p. $90^{\circ}/15$ mm., D_4^{25} 1.5669, n_{H_a} 1.50676, n_D 1.51139, n_{H_s} 1.52341, n_{H_v} 1.53401, at 20° . *Lead triethylisopropyl* has b. p. $90^{\circ}/13$ mm., D_4^{25} 1.5812, n_{H_a} 1.5131, n_D 1.5181, $n_F - n_C$ 0.01773, $n_G - n_C$ 0.02884, at 20° . *Lead triethyl-sec.-butyl* has b. p. $103^{\circ}/13$ mm., D_4^{25} 1.5360, n_{H_a} 1.51600, n_D 1.52088, n_{H_s} 1.53310, n_{H_v} 1.54390, at 15° , $n_F - n_C$ 0.01703. *Lead diethyl-n-propylisopropyl* has b. p. $107^{\circ}/17$ mm., D_4^{21} 1.5336, n_{H_a} 1.51047, n_D 1.51524, n_{H_s} 1.52766, n_{H_v} 1.53842, at 22.1° . *Lead diethyldiisopropyl* has b. p. $95.5^{\circ}/14$ mm., D_4^{25} 1.5358, n_{H_a} 1.51375, n_D 1.51870, n_{H_s} 1.53129, n_{H_v} 1.54245, at 15.9° . *Lead diethyl-n-propyl-sec.-butyl* has b. p. $115.5^{\circ}/14.5$ mm., $D_4^{20.1}$ 1.4962, n_{H_a} 1.51235, n_D 1.51698, n_{H_s} 1.52896, n_{H_v} 1.53939 at 20.1° . *Lead triethyl-sec.-amyl* has b. p. $121^{\circ}/17$ mm., D_4^{21} 1.4906, n_{H_a} 1.51065, n_D 1.51537, n_{H_s} 1.52717, n_{H_v} 1.53712, at 21° . *Lead dimethyl-sec.-butyliso-amyl*, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot PbMe_2 \cdot CHMeEt$, has b. p. $111.5-112.5^{\circ}/14$ mm., D_4^{25} 1.4709, n_{H_a} 1.50125, n_D 1.50571, n_{H_s} 1.51686, n_{H_v} 1.52675, at 22° . *Lead diethyl-n-propyl-sec.-amyl* has b. p. $121^{\circ}/12$ mm., $D_4^{19.4}$ 1.4554, n_{H_a} 1.50948, n_D 1.51393, n_{H_s} 1.52551, n_{H_v} 1.53571, at 19.4° .

All the densities are reduced to vacuum standard. J. C. W.

Cracking of an Aromatic Base Oil. The Temperature Factor at Constant Rate under Pressure. GUSTAV EGLOFF and ROBERT J. MOORE (*J. Ind. Eng. Chem.*, 1917, 9, 40-42).—Solvent naphtha was subjected to thermal decomposition in a steel tube, at temperatures of 500° , 600° , 650° , 700° , 750° , and 800° under a pressure of 11 atmospheres and a rate of flow of 15 gallons per hour. The highest yields of benzene in the recovered oil were obtained at the higher temperatures, with a maximum of 42.5% at 800° . The maximum yield of toluene was 39.9% at 750° , but as at the higher temperatures the percentage of recovered oil rapidly falls, the actual yield of toluene is the greater when calculated on the naphtha used, namely, 20.6% at 750° , as against 15.9% of benzene at 800° . The mechanism of the reaction is one of demethylation, similar to that produced by the action of aluminium chloride on alkylbenzene derivatives. Compared with the yields of benzene and toluene obtained by the cracking of paraffin and naphthene oils, the results obtained with solvent naphtha indicated that it is the most satisfactory oil to use for the production of these hydrocarbons, the benzene being 140% and the toluene 350% in excess of that obtained from the former oils.

G. F. M.

Molecular Organic Compounds. MICHELE GIUA (*Gazzetta*, 1917, 47, i, 74—86. Compare A., 1916, i, 266).—The points discussed in this paper comprise the historical development of the idea of molecular compounds, the nature and classification of molecular organic compounds, and labile molecular compounds.

T. H. P.

[Preparation of Diphenyl.] A. J. GRANT and C. JAMES (*J. Amer. Chem. Soc.*, 1917, 39, 933—937).—See this vol., ii, 317.

Formation of Aniline from Ammonia and Benzene at High Temperatures, and in the Presence of Contact Catalysts. J. P. WIBAUT (*Ber.*, 1917, 50, 541—546).—Meyer and Tanzen have shown that a small yield of aniline can be obtained by passing a mixture of benzene and ammonia through a tube heated at 550°, the reaction being reversible (A., 1913, i, 1294). Sabatier and Senderens have also shown that the reverse change, the conversion of aniline into benzene and ammonia by the action of hydrogen, takes place readily at 250° in the presence of nickel, and so the author has thought it to be of interest to find, if possible, a catalyst for the forward change.

Contrary to Meyer and Tanzen's experience, he finds that no appreciable amount of aniline is formed in a porcelain tube below 700° unless reduced iron, nickel, or copper is present. Even then the yield of aniline is very minute. The best result was obtained by passing a stream of ammonia through benzene at 75°, and then through an iron tube about 60 cm. long packed with reduced nickel, iron, and asbestos, heated at 550—560°, when 0.16 gram of acetanilide was produced from the 200 grams of condensed vapour.

J. C. W.

Action of Aromatic Amines on Aliphatic Acids. E. DE'CONNO (*Gazzetta*, 1917, 47, i, 93—132).—A number of anilides of higher aliphatic acids have been prepared by heating the acid (1 mol.) with the aromatic amine (1 mol.) for five hours at 230° in a sealed tube freed from air by means of a mercury pump (compare A., 1916, i, 788). The anilides thus obtained are crystalline and melt to dark yellow liquids, with the exception of those of linolenic acid, which are liquid at the ordinary temperature. In all cases they are completely hydrolysed when heated in a sealed tube at 150° with concentrated hydrochloric acid. All the amides yet prepared distil unaltered under a pressure of 10 mm., and the increment of the boiling point in a homologous series is at least 10°, so that fractional distillation in a vacuum should result in sharp separation of the constituents of a mixture of such amides.

Myristoanilide, $C_{13}H_{27} \cdot CO \cdot NHPh$ (compare Masino, A., 1880, 460), forms slender needles, m. p. 81.5°, b. p. 113°/10 mm.

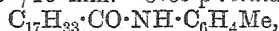
Palmitoanilide, $C_{15}H_{31} \cdot CO \cdot NHPh$ (compare Dellschaft, A., 1902, i, 142; Hell and Jordanoff, A., 1891, 820, 821), forms long, hard, silky needles, m. p. 88.5°, b. p. 132.5°/10 mm.

Stearoanilide, $C_{17}H_{33}\cdot CO\cdot NHPh$ (compare Pébal, *Annalen*, 1854, 91, 138; Claus and Häfelin, A., 1897, i, 187), forms radiating masses of slender, shining, white needles, m. p. 88° , b. p. $153\cdot5^\circ/10$ mm.

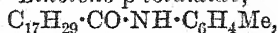
Arachioanilide, $C_{19}H_{39}\cdot CO\cdot NHPh$ (compare Baczewski, A., 1897, i, 11), forms long, white, matted needles, m. p. $91\cdot5^\circ$, b. p. $172^\circ/10$ mm.

Oleoanilide, $C_{17}H_{33}\cdot CO\cdot NHPh$, forms nacreous masses of slender, shining, colourless needles, m. p. 41° , b. p. $143\cdot5^\circ/10$ mm. Erucioanilide, $C_{21}H_{41}\cdot CO\cdot NHPh$ (compare Reimer and Will, A., 1887, 233), forms masses of minute, shining needles, m. p. 55° , b. p. $181^\circ/10$ mm. *Linolenoanilide*, $C_{17}H_{29}\cdot CO\cdot NHPh$, forms a faint yellow, neutral, oily, limpid liquid.

Myristo-p-toluidide, $C_{13}H_{27}\cdot CO\cdot NH\cdot C_6H_4Me$, forms nacreous flakes composed of long, slender needles, m. p. 84° , b. p. $121\cdot5^\circ/10$ mm. *Palmito-p-toluidide*, $C_{15}H_{31}\cdot CO\cdot NH\cdot C_6H_4Me$ (compare Claus and Häfelin, *loc. cit.*), forms nacreous masses of long, silky needles, m. p. $93\cdot5^\circ$, b. p. $140^\circ/10$ mm. *Stearo-p-toluidide*, $C_{17}H_{33}\cdot CO\cdot NH\cdot C_6H_4Me$, forms nacreous masses of slender, white needles, m. p. $95\cdot5^\circ$, b. p. $161\cdot5^\circ/10$ mm. *Aracho-p-toluidide*, $C_{19}H_{39}\cdot CO\cdot NH\cdot C_6H_4Me$, forms long, white needles, m. p. 96° , b. p. $189\cdot5^\circ/10$ mm. *Oleo-p-toluidide*,

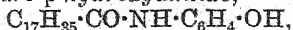


forms felted masses of minute, shining needles, m. p. $42\cdot5^\circ$, b. p. $156\cdot5^\circ/10$ mm. *Erucio-p-toluidide*, $C_{21}H_{41}\cdot CO\cdot NH\cdot C_6H_4Me$, forms nacreous masses of minute, shining needles, m. p. $57\cdot5^\circ$, b. p. $192\cdot5^\circ/10$ mm. *Linoleno-p-toluidide*,



forms a clear, almost colourless oil.

Myristo-m-xylidide, $C_{13}H_{27}\cdot CO\cdot NH\cdot C_6H_3Me_2$, forms mammillary masses of long, soft needles, m. p. 93° , b. p. $127\cdot5^\circ/10$ mm. *Palmito-m-xylidide*, $C_{15}H_{31}\cdot CO\cdot NH\cdot C_6H_3Me_2$, forms mammillary masses of soft, almost colourless needles, m. p. $97\cdot5^\circ$, b. p. $148^\circ/10$ mm. *Stearo-m-xylidide*, $C_{17}H_{33}\cdot CO\cdot NH\cdot C_6H_3Me_2$ (compare Claus and Häfelin, *loc. cit.*), forms minute, white needles, m. p. 102° , b. p. $159\cdot5^\circ/10$ mm. *Aracho-m-xylidide*, $C_{19}H_{39}\cdot CO\cdot NH\cdot C_6H_3Me_2$, forms masses of shining, white needles, m. p. 99° , b. p. $181\cdot5^\circ/10$ mm. *Oleo-m-xylidide*, $C_{17}H_{33}\cdot CO\cdot NH\cdot C_6H_3Me_2$, forms masses of minute, shining, colourless needles, m. p. $59\cdot5^\circ$, b. p. $167\cdot5^\circ/10$ mm. *Erucio-m-xylidide*, $C_{21}H_{41}\cdot CO\cdot NH\cdot C_6H_3Me_2$, forms gum-like masses of matted, minute needles, m. p. $68\cdot5^\circ$, b. p. $190^\circ/10$ mm. *Linoleno-m-xylidide*, $C_{17}H_{29}\cdot CO\cdot NH\cdot C_6H_3Me_2$, is an oily, almost colourless liquid. *Myristo-p-hydroxyanilide*, $C_{13}H_{27}\cdot CO\cdot NH\cdot C_6H_4\cdot OH$, forms minute, shining, colourless needles, m. p. 113° , b. p. $206^\circ/10$ mm. *Palmito-p-hydroxyanilide*, $C_{15}H_{31}\cdot CO\cdot NH\cdot C_6H_4\cdot OH$, forms matted masses of minute, shining needles, m. p. 131° , b. p. $225\cdot5^\circ/10$ mm. *Stearo-p-hydroxyanilide*,



forms long, colourless needles, m. p. 132° , b. p. $239\cdot5^\circ/10$ mm.

Aracho-p-hydroxyanilide, $C_{19}H_{30} \cdot CO \cdot NH \cdot C_6H_4 \cdot OH$, forms matted masses of long, white needles, m. p. 115° , b. p. $259^\circ/10$ mm. *Oleo-p-hydroxyanilide*, $C_{17}H_{33} \cdot CO \cdot NH \cdot C_6H_4 \cdot OH$, forms slender, white needles, m. p. 80° , b. p. $251.5^\circ/10$ mm. *Eruco-p-hydroxyanilide*, $C_{21}H_{41} \cdot CO \cdot NH \cdot C_6H_4 \cdot OH$, forms silver-white crusts of minute, shining needles, m. p. 114° , b. p. $282^\circ/10$ mm.

Myristo-p-methoxyanilide, $C_{19}H_{37} \cdot CO \cdot NH \cdot C_6H_4 \cdot OMe$, forms shining, colourless needles, m. p. 101.5° , b. p. $215.5^\circ/10$ mm. *Palmito-p-methoxyanilide*, $C_{15}H_{31} \cdot CO \cdot NH \cdot C_6H_4 \cdot OMe$, forms long, colourless needles, m. p. 108° , b. p. $238^\circ/10$ mm. *Stearo-p-methoxyanilide*, $C_{17}H_{35} \cdot CO \cdot NH \cdot C_6H_4 \cdot OMe$, forms minute, white needles, m. p. 104° , b. p. $259.5^\circ/10$ mm. *Aracho-p-methoxyanilide*,

$C_{19}H_{39} \cdot CO \cdot NH \cdot C_6H_4 \cdot OMe$, forms long, white needles, m. p. 106° , b. p. $281.5^\circ/10$ mm. *Oleo-p-methoxyanilide*, $C_{17}H_{33} \cdot CO \cdot NH \cdot C_6H_4 \cdot OMe$, forms minute, colourless needles, m. p. 67° , b. p. $262^\circ/10$ mm. *Eruco-p-methoxyanilide*, $C_{21}H_{41} \cdot CO \cdot NH \cdot C_6H_4 \cdot OMe$, forms minute, shining, colourless needles, m. p. 85° , b. p. $287.5^\circ/10$ mm.

Myristo-p-ethoxyanilide, $C_{23}H_{37}O_2N$, forms minute, silky needles, m. p. 108° , b. p. $228.5^\circ/10$ mm. *Palmito-p-ethoxyanilide*, $C_{24}H_{41}O_2N$, forms minute, translucent scales, m. p. 109° , b. p. $250^\circ/10$ mm. *Stearo-p-ethoxyanilide*, $C_{26}H_{45}O_2N$, forms shining, white needles, m. p. 110° , b. p. $269.5^\circ/10$ mm. *Aracho-p-ethoxyanilide*, $C_{28}H_{49}O_2N$, forms minute, shining, white needles, m. p. 111° , b. p. $290^\circ/10$ mm. *Oleo-p-ethoxyanilide*, $C_{26}H_{43}O_2N$, forms minute, shining, colourless needles, m. p. 72° , b. p. $265.5^\circ/10$ mm. *Eruco-p-ethoxyanilide*, $C_{30}H_{51}O_2N$, forms small, silky chips, m. p. 87° , b. p. $288^\circ/10$ mm.

Myristo- α -naphthalide, $C_{13}H_{27} \cdot CO \cdot NH \cdot C_{10}H_7$, forms masses of slender needles, m. p. 110° , b. p. $162.5^\circ/10$ mm. *Palmito- α -naphthalide*, $C_{15}H_{31} \cdot CO \cdot NH \cdot C_{10}H_7$, forms radiating masses of hard, silky needles, m. p. 112.8° , b. p. $182^\circ/10$ mm. *Stearo- α -naphthalide*, $C_{28}H_{43}ON$, forms mammillary masses of short, slender, white needles, m. p. 110.8° , b. p. $205^\circ/10$ mm. *Aracho- α -naphthalide*, $C_{30}H_{47}ON$, forms minute needles, m. p. 99° , b. p. $221.5^\circ/10$ mm. *Oleo- α -naphthalide*, $C_{28}H_{41}ON$, forms minute needles, m. p. 60° , b. p. $190.5^\circ/10$ mm. *Eruco- α -naphthalide*, $C_{32}H_{49}ON$, forms masses of minute, shining needles, m. p. 73° , b. p. $230^\circ/10$ mm.

Myristo- β -naphthalide, $C_{24}H_{35}ON$, forms mammillary masses of long, slender needles, m. p. 108° , b. p. $179^\circ/10$ mm. *Palmito- β -naphthalide*, $C_{26}H_{39}ON$, forms mammillary masses of small, acicular crystals, m. p. 109° , b. p. $198.5^\circ/10$ mm. *Stearo- β -naphthalide*, $C_{28}H_{45}ON$, forms nacreous masses of slender, white needles, m. p. 109° , b. p. $220.5^\circ/10$ mm. *Aracho- β -naphthalide*, $C_{30}H_{47}ON$, forms shining, white needles, m. p. 112° , b. p. $239^\circ/10$ mm. *Oleo- β -naphthalide*, $C_{28}H_{41}ON$, forms shining masses of nacreous scales, m. p. 169.2° , b. p. $215.5^\circ/10$ mm. *Eruco- β -naphthalide*, $C_{32}H_{49}ON$, forms shining, colourless needles, m. p. 87° , b. p. $247.5^\circ/10$ mm.

Myristo-p-phenylenediamide, $C_6H_4(NH \cdot CO \cdot C_{13}H_{27})_2$, forms

minute, pale grey needles, m. p. 162.5° , b. p. $186.5^{\circ}/10$ mm. *Palmito-p-phenylenediamide*, $C_{33}H_{63}O_2N_2$, forms short, almost colourless, shining needles, m. p. 181.5° , b. p. $208^{\circ}/10$ mm. *Stearo-p-phenylenediamide*, $C_{42}H_{76}O_2N_2$, forms minute, white needles, m. p. 179.5° , b. p. $229.5^{\circ}/10$ mm. *Aracho-p-phenylenediamide*, $C_{46}H_{84}O_2N_2$, forms minute needles, m. p. 139.8° , b. p. $250^{\circ}/10$ mm. *Oleo-p-phenylenediamide*, $C_{42}H_{72}O_2N_2$, forms minute needles, m. p. 158.7° , b. p. $224.5^{\circ}/10$ mm. *Eruco-p-phenylenediamide*, $C_{50}H_{88}O_2N_2$, forms minute, grey needles, m. p. 151° , b. p. $263^{\circ}/10$ mm. T. H. P.

Polymorphism of 2:6-Dinitro-4-toluidine. I. and II.

E. ARTINI (*Atti R. Accad. Lincei*, 1917, [v], 26, i, 392—400, 420—424).—This compound, prepared by Körner and Contardi by reducing 2:4:6-trinitrotoluene with ammonium sulphide, exists in four distinct crystalline phases, with the following properties.

The δ -modification, obtained by slow evaporation of a cold saturated solution in a mixture of ether and alcohol, forms prismatic crystals of the rhombic system (? bipyramidal class), $a:b=0.7935:1$, $D\ 1.524$, showing marked pleochroism.

The γ -phase, which is easily obtained by evaporation of cold saturated solutions in ethyl acetate or acetone, either alone or mixed with alcohol, forms crystals of varying habit, but mostly short and stout and belonging to the pinacoidal class of the triclinic system, $a:b:c=0.8389:1.21764$, $\alpha=93^{\circ}26'$, $\beta=89^{\circ}00'$, $\gamma=89^{\circ}33'$, $D\ 1.497$; twinning is frequent and pleochroism evident.

The β -form, which is often obtained with the γ -modification from ethyl acetate or acetone and is also deposited on very slow cooling of a boiling alcoholic solution, forms rhombic crystals of the bipyramidal class, $a:b:c=0.8557:1.1119$, $D\ 1.495$, and shows distinct pleochroism.

In spite of their different degrees of symmetry, the γ - and β -modifications are markedly similar in external form, and also exhibit various morphological and physical relations and frequently occur associated.

The δ -phase is metastable, at any rate as far as temperatures a few degrees below 0° , and if it is deposited in a flask from a mixture of ether and alcohol and, when the crystallisation has proceeded sufficiently far, the flask is stoppered, the yellow δ -needles gradually pass into solution and are replaced by the triclinic γ -form. The latter is the most stable at the ordinary or a lower temperature and the β -phase is metastable towards the γ -phase at the ordinary temperature.

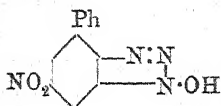
The fourth or α -phase forms pale orpiment-yellow crystals and arises when either of the preceding modifications is heated at 148° , its region of stability extending only from 148° to 173° , the melting point. When cooled below 148° it undergoes immediate transformation into the β -phase.

The conditions of equilibrium between the different phases are represented graphically. T. H. P.

Some New Derivatives of Diphenyl. W. BORSCHKE and B. G. B. SCHOLTEN (*Ber.*, 1917, **50**, 596—611).—Now that *o*-hydroxy- and *oo'*-dihydroxy-diphenyl are commercial products, material has become available for a resumption of an investigation on diphenyl derivatives begun in 1900 (*A.*, 1900, i, 24, 594).

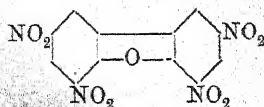
Derivatives of o-Hydroxydiphenyl.—2-Phenylbenzoquinone-4-oxime, which was originally the precursor of the *o*-hydroxydiphenyl, is best obtained from this by the action of nitrous acid. It may be oxidised by alkaline potassium ferricyanide or hydrogen peroxide to 5-nitro-2-hydroxydiphenyl (*ibid.*, 594), and this converted by methylation into 5-nitro-2-methoxydiphenyl, pale yellow, friable needles, m. p. 95—96°. The latter can be obtained readily by the nitration of *o*-methoxydiphenyl (methylation of the phenol; b. p. 159—160°/18 mm.), but the free phenol yields almost exclusively 3:5-dinitro-2-hydroxydiphenyl, m. p. 203—204°. The phenol couples with benzenediazonium chloride, giving 2-hydroxy-5-benzeneazodiphenyl, yellow needles, m. p. 94—95°, and 2-hydroxy-3:5-bisbenzeneazodiphenyl, brown needles, m. p. 157°. The former azo-compound is readily reduced by sodium hyposulphite to 5-amino-2-hydroxydiphenyl, m. p. 201°.

3:5-Dinitro-2-hydroxydiphenyl forms a *p*-toluenesulphonate, long, stout, yellow needles, m. p. 147—148°, and also 2-chloro-3:5-dinitrodiphenyl, yellow leaflets, m. p. 119°, when heated with *p*-toluenesulphonyl chloride and dimethylaniline (a reaction of *op*-dinitrophenols discovered by Ullmann and Náday, *A.*, 1908, i, 525). The *o*-chloro-derivative reacts with alcoholic ammonia at 100° to form 3:5-dinitro-2-aminodiphenyl, golden-yellow leaflets, m. p. 182°; with aniline, very sluggishly, to give 3:5-dinitro-2-anilindiphenyl, bright red needles, m. p. 130°; and with hydrazine hydrate to yield 6-nitro-4-phenylbenzaziminol (annexed formula), which crystallises in yellow leaflets, decomp. 229°.



Derivatives of oo'-Dihydroxydiphenyl.—This phenol reacts with acetic acid and sodium nitrite to form 2:2'-diphenyldiquinone-4:4'-dioxime (annexed formula) as a dark yellow, microcrystalline powder which decomposes briskly at 227—228°. This may be reduced to 5:5'-diamino-2:2'-dihydroxydiphenyl, but the amine is more readily obtained by reducing 5:5'-bisbenzeneazo-2:2'-diphenol (Robertson and Brady, *T.*, 1913, **103**, 1481) with sodium hyposulphite. The diamine yields the 2:2'-diphenyldiquinone, m. p. 196°, on oxidation.

3:5:3':5'-Tetranitro-2:2'-diphenol does not behave in the normal way on heating with *p*-toluenesulphonyl chloride and dimethylaniline. It yields 1:3:6:8-tetranitrodiphenylene oxide (annexed formula), which crystallises in lustrous, pale brown needles, m. p. 252.5°.



2:2'-Dimethoxydiphenyl yields 5:5'-dinitro-2:2'-dimethoxydiphenyl, slender,

yellow needles, m. p. 263° , when warmed with nitric (D 1.39) and glacial acetic acids, but when first sulphonated and then warmed with fuming nitric and sulphuric acids, it forms 3:5:3':5'-*tetra-nitro-2:2'-dimethoxydiphenyl*, which crystallises in broad, yellow needles, m. p. $177-178^{\circ}$. The latter yields the well-known 1:3:6:8-tetranitrocarbazole, m. p. 268° , when heated with alcoholic ammonia at $140-150^{\circ}$, but this synthesis offers the first proof of the constitution of the compound.

Derivatives of pp'-Dihydroxydiphenyl.—3:5:3':5'-Tetranitro-4:4'-dihydroxydiphenyl is obtained by adding concentrated nitric acid to diazotised benzidine and warming. It only forms a *di-p-toluenesulphonate*, yellow leaflets, m. p. 267° (decomp.), when treated by the above method of Ullmann and Náday, no trace of the tetranitro-4:4'-dichlorodiphenyl being produced. Neither could any more than the known 2:2'-dinitro-compound be obtained by nitrating 4:4'-dichlorodiphenyl. The above ester is transformed by boiling aniline into 3:5:3':5'-*tetranitro-4:4'-dianilinodiphenyl*, which crystallises in fiery-red needles, m. p. 271° .

Derivatives of mm'-Dichlorodiphenyl.—This oil yields 5:5'-dichloro-2:2'-dinitrodiphenyl when carefully warmed with fuming nitric acid, but 5:5'-*dichloro-2:4:2':4'-tetranitrodiphenyl*, yellow leaflets, m. p. 189° , when warmed with a mixture of sulphuric and fuming nitric acids. The latter yields the 5:5'-*diamine*, reddish-brown crystals, m. p. 297° , and an additive compound of aniline and the 5:5'-dianilino-derivative, $C_{12}H_4(NHPh)_2(NO_2)_4 \cdot NH_2Ph$, stout, dark red needles, m. p. 215° . J. C. W.

The State of Saturation of Chromophores. HUGO KAUFFMANN (*Ber.*, 1917, 50, 630—637).—The author issues a warning against a false idea of the importance of the degree of unsaturation in connexion with colour theories. There is a tendency in some quarters (compare Ley, this vol., i, 261, and Lifschitz, *Zeitsch. wiss. Photochem.*, 1916, 16, 101) to expect that a lowering of the intensity of colour would follow if the degree of unsaturation of the chromophore is lowered. Even when such difficulties are ignored as the question as to what "unsaturation" really means, what kind of unsaturation is authoritative in optical problems, why it is that ethylene is colourless whilst more saturated stilbene derivatives are coloured, why *m*-nitroaniline is coloured but *m*-dinitrobenzene colourless, why colourless aniline and almost colourless 1:3:5-trinitrobenzene should form a red compound, there are still, even within narrow limits, cases in which colour is actually enhanced when the degree of unsaturation is lessened.

It is known, for example, that the degree of saturation of an ethylene linking is raised by the proximity of a phenyl, carboxyl or carbethoxyl, or cyano-group in the order given, but in three cases the effect on the colour is quite the opposite to the expected one. In the series $R \cdot CH : CHPh$, $R \cdot CH : CPh \cdot CO_2H$, $R \cdot CH : CPh \cdot CN$ [$R = C_6H_3(OMe)_2, 2:5$]; the colours are white, pale greenish-yellow, and bright greenish-yellow; with the compounds of the same radicle, $R \cdot CH : CPh \cdot CN$, $R \cdot CH : C(CN) \cdot CO_2Et$, $R \cdot CH : C(CN)_2$, the colours are greenish-yellow, lemon or orange-red (two forms), and

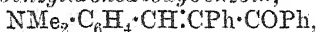
orange-yellow; whilst in the series of para-derivatives of dimethylaniline, $R \cdot CH : CHBz$, $R \cdot CH : CPhBz$, $R \cdot CH : CBz \cdot CN$, $R \cdot CH : CPh \cdot CN$, $R \cdot CH : C(CN) \cdot CO_2Et$, $R \cdot CH : C(CN)_2$, the compounds are orange-red, chrome-yellow, brick-red, lemon-yellow, orange, and brick-red respectively.

It is therefore emphasised that whilst "unsaturation" is a factor which confers chromophoric properties on atomic groups, it is in no sense the factor which determines the degree of the chromophoric activity.

Some new compounds have been prepared [with KARL BURR, EMIL MEYER, and ADOLF JEUTER]. *ω-Nitro-2:5-dimethoxystyrene*, from the dimethoxybenzaldehyde and nitromethane, forms long, orange-red, fluorescent needles, m. p. 118° . *2:5-Dimethoxy-β-nitro-Δ²-propenylbenzene*, $NO_2 \cdot CMe \cdot CH \cdot C_6H_3(OMe)_2$, from nitroethane, crystallises in slender, orange-yellow needles, m. p. 75° . *ω-Nitro-2:5-dimethoxystilbene*, $NO_2 \cdot CPh \cdot CH \cdot C_6H_3(OMe)_2$, from phenylnitromethane, forms orange-yellow crystals, m. p. 124° . The colours in these cases are therefore lessened in intensity as the ethylene linking becomes more saturated.

2:5-Dimethoxy-α-phenylcinnamic acid, from the aldehyde and sodium phenylacetate and acetic anhydride, forms pale greenish-yellow crystals, m. p. 192° .

p-Dimethylaminobenzylidenedeoxybenzoïn,



crystallises in chrome-yellow needles, m. p. 167° .

J. C. W.

Aminophenylethylcarbinol [*β*-Amino-*α*-phenylpropyl Alcohol]. AUGUST EBERHARD (*Arch. Pharm.*, 1917, 255, 140—150).—In order to synthesise ephedrine or *ψ*-ephedrine, it is necessary to methylate *β*-amino-*α*-phenylpropyl alcohol. Preliminary work on this reaction has shown that much material will be required in order to obtain a pure product (Calliess, A., 1912, i, 365; Eberhard, A., 1915, i, 834). It is now found that the carbinol can best be prepared from *α*-aminopropiophenone by reduction with hydrogen in the presence of palladinised charcoal. The methylation of the hydramine will be described later, but some new derivatives have been obtained in the meantime and others revised.

β-Amino-*α*-phenylpropyl alcohol crystallises in flat needles, m. p. 101° , and yields the following compounds: a hydrochloride, m. p. 191° ; two isomeric but not interchangeable aurichlorides (bundles of silky, yellow needles, m. p. 130° , and hard, yellowish-red rosettes, m. p. 172°); two platinichlorides (yellowish-red needles, with $2H_2O$, m. p. 187 — 188° , and anhydrous, brownish-red bundles, m. p. 196°); a benzoyl derivative, m. p. 142° (Behr-Bregowski, A., 1897, i, 460); and a *dibenzoyl* compound, $OBz \cdot CHPh \cdot CHMe \cdot NHBz$, white flocks, m. p. 162° .

J. C. W.

***p*-Lactylaminobenzoic Acid**. E. SALKOWSKI (*Ber.*, 1917, 50, 637—641).—As another attempt to prepare a soluble, but physiologically active, derivative of ethyl *p*-aminobenzoate (compare A.,

1916, i, 815), the drug ("anæsthesine") has been converted into the lactyl derivative, by heating with an excess of lactic acid. The new ester is a brown syrup which is neither soluble nor possessed of anæsthetic properties. The free *p*-lactylaminobenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{OH}$, obtained by hydrolysis of the crude product or, better, by heating together the free acids, crystallises as a mass of woolly needles, m. p. 215° , and yields a white *silver*, and a microcrystalline *copper* salt. It gives no coloration with ferric chloride (distinction from *p*-aminobenzoic acid); it is gradually hydrolysed by boiling sodium hydroxide, but not by sodium carbonate. J. C. W.

Synthesis of Phloretin, and Preparation of the Nitriles of Phenolcarboxylic Acids. EMIL FISCHER and OSMAN NOURI (*Ber.*, 1917, 50, 611—623).—The nitriles of phenolcarboxylic acids can be obtained by converting the acetyl compounds into the amides, dehydrating these with phosphorus chlorides, and finally removing the acetyl groups again by a mild hydrolysis. By such a means, phloretonitrile has been prepared and then converted into phloretin by Hoesch's new method for the synthesis of phenolic ketones (compare A., 1915, i, 820).

Phloretic acid (β -*p*-hydroxyphenylpropionic acid) is most conveniently obtained by the hydrolysis of phloridzin, and its esters by means of the alcohols and sulphuric acid. The ethyl ester has m. p. $43\text{--}44^\circ$, b. p. $193^\circ/18$ mm. (corr.); the *methyl* ester crystallises in large, thin tablets, m. p. $40\text{--}41^\circ$ (corr.), b. p. $186\text{--}187^\circ/17$ mm. (corr.). The amide, m. p. $127\text{--}128^\circ$, is best obtained from the methyl ester. *Acetylphloretamide* (β -*p*-acetoxyphenylpropionamide) is formed by the action of acetic anhydride and pyridine on the amide; it crystallises in elongated, thin plates, m. p. $133\text{--}134^\circ$ (corr.), and yields the corresponding *nitrile*, b. p. $170\text{--}175^\circ/0.25$ mm., when heated with chloroform and phosphoryl chloride. *Phloretonitrile* (β -*p*-hydroxyphenylpropionitrile) is obtained from this by hydrolysis with cold aqueous-alcoholic sodium hydroxide, in colourless prisms, m. p. $58\text{--}59^\circ$. When an ethereal solution of the acetylphloretonitrile and phloroglucinol is treated with hydrogen chloride in the presence of zinc chloride, condensation takes place as in Hoesch's method, and the intermediate ketone-imide salt can be hydrolysed to a mixture of free phloretin and its acetyl derivative. A further treatment with *N*-sodium hydroxide in the absence of air serves to decompose the acetate, and phloretin, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{OH})_3$, identical with the phloretin of phloridzin may be isolated.

Methyl *p*-coumarate, m. p. $139\text{--}140^\circ$ (corr.), is converted into *p*-coumaramide, microscopic leaflets, m. p. $193\text{--}194^\circ$ (corr.), and the *acetyl* derivative of this, m. p. $189\text{--}191^\circ$ (corr.), into *p*-acetoxycinnaonitrile, m. p. $117\text{--}118^\circ$ (corr.), and finally into *p*-coumaronitrile, long prisms, m. p. $138\text{--}139^\circ$ (corr.), by the above methods.

Similarly, gallamide is transformed into the triacetate, *triacetyl-gallonitrile*, long needles or prisms, m. p. $129\text{--}130^\circ$ (corr.), and

finally *gallouitrile*, which crystallises from water in very long needles, $1\text{H}_2\text{O}$, m. p. 223° (corr.).

J. C. W.

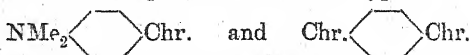
Phenylpyruvic Acid. (MLLE.) R. HEMMERLÉ (*Ann. Chim.*, 1917, [ix], 7, 226—276).—A full account of work of which a short description has appeared (compare A., 1916, i, 485). Certain new compounds are described, namely, *sodium phenylpyruvate*, $\text{C}_9\text{H}_7\text{O}_3\text{Na}\cdot\text{H}_2\text{O}$; the *methyl ester*, m. p. 75° ; the *ethyl ester*, m. p. 45° ; and the *acetate*, m. p. 168° , of phenylpyruvic acid; the *acetate*, m. p. 125° , of benzylpyruvic acid; *methyl diphenyldipyrivate*, m. p. 101° ; *ethyl diphenyldipyrivate*, m. p. 102° ; the *keto-alcohol*, $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{OH}$, corresponding with α -keto- β -diphenylbutyrolactone (compare Erlenmeyer, A., 1904, i, 1015); α -keto- β -phenylbutyrolactone, m. p. 202° , and its *semicarbazone*, m. p. 220° (decomp.), and its *methyl ether*, m. p. 84° .

W. G.

An Ethoxy- β -naphthoylpropionic Acid. M. GIUA (*Gazzetta*, 1917, 47, i, 89—92. Compare A., 1914, i, 962).—The action of succinic anhydride on α -naphthyl ethyl ether in carbon disulphide solution and in the presence of aluminium chloride yields an *ethoxy- β -naphthoylpropionic acid*, $\text{OEt}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which forms pale yellow needles, m. p. 198° , gives a greenish-yellow coloration with concentrated sulphuric acid, and yields *o*-phthalic acid on oxidation with alkaline permanganate solution; the acid is probably 5-ethoxy- β -2-naphthoylpropionic acid. Its *methyl ester* forms shining, white plates, m. p. 70 — 71° .

Methyl β -2-naphthoylpropionate (compare A., 1914, i, 962), $\text{C}_{15}\text{H}_{14}\text{O}_3$, forms white, prismatic crystals, m. p. 74° . T. H. P.

Chromophores with Auxochromic Functions. HUGO KAUFFMANN (*Ber.*, 1917, 50, 515—529).—The colour and fluorescence of a number of compounds of the two types:



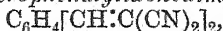
(Chr.=chromophore) have been investigated. It is a well-known fact that *p*-dinitrobenzene is no more coloured than nitrobenzene, but that *p*-dimethylaminonitrobenzene, containing an auxochrome, is bright yellow. Certain cases of styryl derivatives have now been found, however, in which the association of two of these chromophores in compounds of the type II makes for the enhancement of colour over the monostyryl derivatives or even over the corresponding *p*-dimethylaminostyryl derivatives of type I. In these cases, therefore, the styryl complex exerts auxochromic functions; indeed, it sometimes happens that the auxochrome effect is more pronounced than that displayed by the *p*-dimethylamino-group. The chief argument, however, for the exertion of auxochrome activities by these chromophores is that the compounds display brilliant fluorescence, which is in accordance with the rule that the introduction of a second auxochrome in the para-position with respect to another makes for a strongly fluorescent di-derivative.

The following summary illustrates these points. The data refer to the solid compounds.

Chromophore.	NMe ₂ ·C ₆ H ₄ ·Chr.		Chr·C ₆ H ₄ ·Chr.	
	Colour.	Fluorescence.	Colour.	Fluorescence.
·CH:CHPh	White	Moderately strong greenish-blue	Pale yellow	Strong yellowish-green
·CH:CPh·CN	Lemon-yellow	Intense vivid greenish-yellow	Lemon-yellow	Intense yellow
·CH:C(CN)·CO ₂ Et.	Orange	Vivid orange	Pale greenish-yellow	Vivid yellowish-green
·CH:C(CN) ₂	Brick red	Strong orange-red	Yellow	Strong yellow
·CH:C(CN)·COPh..	Brick red	Vivid brick-red	Orange-yellow	Very faint yellow
·CH:C<CO>C ₆ H ₄	Deep red	Moderate purple-red	Orange	Strong orange

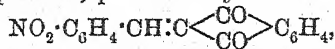
Most of the compounds were obtained by the condensation of the appropriate aldehydes and methylene compounds.

[With ADOLF JEUTTER.]—*p*-Distyrylbenzene, C₆H₄(CH:CHPh)₂, is obtained by the action of terephthalaldehyde on magnesium benzyl chloride, the intermediate carbinol being deprived of the elements of water by heating with acetyl chloride and then alone at 270°. It forms pale yellow crystals, m. p. 258°. *ω*ω'-Dicyano-*p*-distyrylbenzene, C₆H₄(CH:CPh·CN)₂, yellow crystals, m. p. 242°, is obtained from terephthalaldehyde and benzyl cyanide. Ethyl terephthalylidenedicyanoacetate, C₆H₄[CH:C(CN)·CO₂Et]₂, from terephthalaldehyde and ethyl cyanoacetate, forms pale greenish-yellow needles, m. p. 201°. Terephthalylidenedimalononitrile,



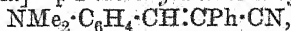
decomposes at 212°. Terephthalylidenedicyanoacetophenone, C₆H₄(CH:CPh·CN)₂, has m. p. 224°. Terephthalylidenediindandione forms orange needles, m. p. above 300°.

Phenyl cyano-styryl ketone forms white crystals, m. p. 84°; phenyl cyano-*p*-methoxystyryl ketone crystallises in pale yellow needles, m. p. 104°; phenyl cyano-*p*-dimethylaminostyryl ketone, m. p. 162°, is brick-red, and forms a white salt with hydrogen chloride gas or solution; phenyl cyano-*p*-nitrostyryl ketone crystallises in pale yellow scales, m. p. 140°; *p*-nitrobenzylideneindandione,



forms greenish-yellow needles, m. p. 229°; *α*-dicyano-*α*-dibenzoylbutadiene, CN·CPh·CH:CH·CPh·CN, from glyoxal and cyanoacetophenone, decomposes at 170–175°, and is white, whereas the terephthalylidene compound in which the –CH:CPh·CN chromophores are separated by the benzene nucleus is orange-yellow.

[With EMIL MEYER.]—*p*-Dimethylamino-*o*-cyanostilbene,



from benzyl cyanide and *p*-dimethylaminobenzaldehyde, forms yellow leaflets, m. p. 136°. Its fluorescence in diffused light or

β -rays is comparable in intensity with that of barium platino-cyanide, but it is not sensitive to Röntgen rays. J. C. W.

Dextro-rotatory Menthyl Iodide. N. I. KURSANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1151—1156).—Gradual hydrolysis of crude menthyl chloride shows that the latter contains, besides the lævo-rotatory stable chloride, at least two unstable stereoisomerides with rotations of opposite signs; the menthyl bromide and iodide obtained by similar methods from menthol probably contain analogous secondary stereoisomerides. Menthyl bromide and iodide are sometimes obtained optically inactive or with a slight dextro-rotation, which may, however, be due to a small proportion of admixed menthene formed as a result of the instability of the menthyl haloid. The author has now succeeded in preparing a menthyl iodide with a pronounced dextro-rotation, which cannot be explained by admixture of menthene.

The method of preparation used was similar to that of Celikov (*ibid.*, 1904, **36**, 784). Menthyl acetate, b. p. 101—102°/15 mm., $\alpha_D - 73.05^\circ$ for 10 cm., prepared by boiling menthol with acetic anhydride, was dissolved in an equal volume of chloroform and the solution saturated with dry hydrogen iodide at -20° . The containing tube was then sealed and left at the ordinary temperature for five days. The resulting menthyl iodide, $C_{10}H_{19}I$, b. p. 122—123°/17 mm., $D_4^{20} 1.3787$, $D_4^{20} 1.3586$, exhibits a dextro-rotation which for three different preparations amounted to $+41.2^\circ$, $+35.13^\circ$, and $+37.62^\circ$ in a 10 cm. tube. The menthene obtained by boiling this menthyl iodide with alcoholic potassium hydroxide exhibits the same physical properties as that derived from lævo-rotatory menthyl haloids. The dimenthyl formed, together with menthene and menthane, when the dextro-rotatory menthyl iodide is boiled with sodium in ethereal solution, is a mixture of the same isomerides as are obtained from the ordinary haloid derivatives of menthol, but the crystalline dimenthyl is formed in comparatively small quantity.

Menthyl iodide has also been prepared, in the same way as from menthyl acetate, from menthyl hydrogen phthalate, the properties of the resulting product being b. p. 121—122°/17 mm., $\alpha_D - 13.44^\circ$ in a 10 cm. tube.

The menthyl bromide obtained by Celikov (*loc. cit.*) has also been investigated further. It has b. p. 98—99°/14 mm., $D_4^{20} 1.1504$, $\alpha_D - 5.20^\circ$ in a 10 cm. tube. When boiled in ethereal solution with sodium, it yields menthane and menthene and crystalline and liquid dimenthyls, both lævo-rotatory.

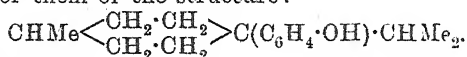
The menthyl bromide prepared by the same method from menthyl hydrogen phthalate has b. p. 106—107°/20 mm., $D_4^{20} 1.1749$, $D_4^{20} 1.1557$, $\alpha_D - 23.35^\circ$ in a 10 cm. tube. T. H. P.

Menthylphenols. N. I. KURSANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1156—1171).—The author showed previously (A., 1915, i, 420) that phenyl menthyl ether is converted by heating with hydrochloric acid at 170° into a mixture of isomeric menthyl-

phenols, and similar mixtures are obtained when the constant or the crude menthyl chloride is heated with phenol. It is now shown that all these mixtures yield urethanes, m. p. 141° and 136° respectively, and also a small quantity of a fraction, m. p. $171-174^{\circ}$; the relative proportions of the different isomerides formed are similar in the various cases.

When crystalline menthylphenol is heated in a sealed tube with hydrochloric acid, part of it decomposes with formation of phenol and optically inactive menthyl chloride, the undecomposed part undergoing isomerisation into a mixture of crystalline and liquid menthylphenols.

As regards the position of the hydroxyphenyl group in the menthylphenols, the optical inactivity of these is explained by the assumption for them of the structure:



Six isomerides of this formula are possible, all having symmetrical molecules. Such tertiary structure for the menthylphenols is confirmed by investigation of the menthyl chloride obtained when menthylphenols are heated with hydrochloric acid. This menthyl chloride is inactive, and, when boiled with alcoholic potash, is transformed into inactive menthene, such transformation being considerably more rapid than that of the unstable secondary menthyl chlorides contained in crude menthyl chloride. Further, the menthyl chloride in question gives instantaneously a copious precipitate with alcoholic silver nitrate solution. All these properties indicate the tertiary nature of the chlorine atom, which may be regarded as occupying the same position as the hydroxyphenol group in the menthylphenols.

The tertiary position of the hydroxyphenyl group in these menthylphenols is confirmed by comparison of the latter with those obtained on boiling menthene hydrochloride with phenol; the urethanes, m. p. 141° and 136° , but not that, m. p. $171-174^{\circ}$, are obtained in this case. When menthene is boiled with phenol in the presence of a small proportion of menthyl chloride, the isomeric menthylphenols formed consist principally of the one giving the urethane, m. p. 141° ; other urethanes, m. p. $115-116^{\circ}$ and m. p. 136° , are also obtained. In this reaction the menthyl chloride reacts with the phenol, liberating hydrochloric acid, which exerts a catalytic effect on the reaction. *Menthylphenyl phenyl ether*, $\text{C}_{10}\text{H}_9 \cdot \text{C}_6\text{H}_4 \cdot \text{OPh}$, prepared by heating the potassium derivative of menthylphenol with iodine and finely-divided copper (compare Ullmann and Sponagel, A., 1905, i, 644; 1907, i, 38), is a viscous, odourless, optically inactive oil, b. p. $223-225^{\circ}/10 \text{ mm.}$, $D_4^{20} 1.0224$. When this ether is heated with magnesium methyl iodide and the product of the reaction decomposed with ice, the resultant products are menthylphenol, phenol, and a menthyltoluene, which gives telephthalic acid on oxidation with dilute nitric acid in a sealed tube. The methyl group of the toluene residue, and consequently the hydroxyl group of the crystalline menthylphenol, thus occupies the para-position to the menthyl residue.

T. H. P.

vulcanised by sulphur or nitro-compounds, although more slowly than caoutchoucs of the normal series, and it is applicable in practice only for certain special purposes.

β -Isoprene caoutchouc, obtained in quantitative yield by the action of a mixture of sodium with barium (or benzoyl) peroxide on pure isoprene at 60—70°, has usually a pale cinnamon colour and is transparent in thin layers; it flakes, but has no stickiness or fluidity, and may be rolled comparatively easily even at 60°. It is an abnormal caoutchouc, its elasticity point being about 80—90°, which is somewhat lower than that of the α -isomeride, and its fatal temperature about -10°.

γ -Isoprene caoutchouc, prepared in small yield (40%) by the action of barium or benzoyl peroxide or an alkaline sulphide or polysulphide at 45—50° for two to four months, is an almost colourless, brittle, amorphous substance, transparent as glass, which cannot be drawn into threads, but is possessed of considerable elasticity and spring; after deformation, it resumes its original form and dimensions almost instantaneously. It is a normal caoutchouc, its elasticity point and fatal temperature being almost identical with those of natural caoutchouc.

δ -Isoprene caoutchouc, prepared from β -myrcene (compare Ostro-misslenski and Koschelev, A., 1916, i, 274), is of the normal series.

ϵ -Isoprene caoutchouc is the name proposed by the author for the caoutchouc obtained in quantitative yield by gently heating isoprene with sodium in an atmosphere of carbon dioxide. It is formed also by the action of the ultra-violet light of the quartz lamp on isoprene in presence of sodium and carbon dioxide. It is a normal isoprene caoutchouc and quite insoluble. This form appears to be a physical isomeride of the normal γ -isoprene caoutchouc, the elasticity points and the fatal temperatures being apparently the same for the two. Towards a mixture of sodium and carbon disulphide isoprene caoutchouc is quite passive, both at the ordinary temperature and on heating.

Recovered caoutchouc is always abnormal, its fatal temperature and elasticity point being relatively high; only above 120° does it regain the elastic properties of ordinary caoutchouc. The process of recovery is evidently accompanied by rearrangement in the nucleus.

α -Erythrene caoutchouc is obtained by heating erythrene alone or with sodium (0.3—0.5%), barium peroxide, sodium and barium peroxide, or first one of these and then the other. When, however, the erythrene is heated in presence of sodium and in an atmosphere of carbon dioxide, it is converted into an insoluble ϵ -caoutchouc analogous to the normal insoluble ϵ -isoprene caoutchouc obtained under similar conditions from isoprene. The isomerism appears to be of a chemical character and conditioned only by the different positions of the ethylene linkings in the molecule. A third isomeride (α') is often formed in small proportion, together with the α -variety, when erythrene is heated with sodium in absence of carbon dioxide. This differs from α -erythrene caoutchouc only in its insolubility, and is a highly elastic, colourless substance, transparent as glass, which

swells in light petroleum, turpentine, etc., and is readily vulcanised under the ordinary conditions given for the vulcanisation of synthetic caoutchoucs (A., 1916, i, 55).

α -Erythrene caoutchouc is a colourless, transparent, elastic, highly resilient substance, which does not stick, and is readily rolled in the hot, but if rolled in the cold requires a slight admixture of a liquid of high boiling point, since otherwise it crumbles between the rolls like factis; after deformation, if not too prolonged, it recovers its form and dimensions almost instantly. This caoutchouc belongs to the normal series, its elasticity point and fatal temperature being somewhat lower than those of Para caoutchouc; thus, at normal temperatures it is more elastic than natural caoutchouc, and it remains elastic when Para caoutchouc reaches its elasticity point. It is vulcanised more rapidly and easily than the natural rubber under ordinary conditions or by means of benzoyl peroxide, nitro-compounds, chlorine, etc. The vulcanised product is highly elastic and resilient and its residual elongation negligible; it is more resistant to deformation than vulcanised natural caoutchouc, but its resistance to shearing is slight. If, before vulcanisation, the caoutchouc is caused to swell by means of albumin or some other substance with colloidal properties, the resultant product corresponds in properties with vulcanised natural caoutchouc.

α -Erythrene-butylene caoutchouc, prepared by the action of sodium on erythrene containing butylenes, closely resembles α -isoprene-amylene caoutchouc.

β -Erythrene-butylene caoutchouc, prepared by heating a toluene solution of the α -isomeride with barium peroxide (0.5–5%) at 60–75° for one to seven days, is not sticky, exhibits great compactness, is somewhat resistant to shearing, cannot be drawn into threads, and is moderately easily rolled in the cold. It belongs to the normal series and is readily vulcanised to a product showing all the properties of vulcanised natural caoutchouc; it dissolves in benzene, light petroleum, turpentine, etc. The isomerisation of the α - to the β -isomeride occurs only if the former contains comparatively little butylenes, erythrene containing 10–15% of the latter being utilisable.

All the caoutchoucs which have been obtained from $\beta\gamma$ -dimethylethythrene (compare Couturier, A., 1893, i, 244; Kondakov, A., 1901, i, 625; Harries, A., 1911, i, 798) have been investigated, and are found to be identical; they usually contain varying proportions of the dimeride and of foreign liquids, which lower the elasticity point and the fatal temperature. The form obtained by the action of sunlight on the monomeride (α') does, indeed, differ from that resulting from the thermopolymerisation of the $\beta\gamma$ -dimethylethythrene (α) by its solubility in various media, but this difference is doubtless conditioned by differences in the physical state, the two being merely colloidal modifications of one and the same hydrocarbon. A number of different catalysts were employed, but in all cases the α -form was obtained in the hot and mostly the α' -form at temperatures up to 20–30°. Further, polymerisation of $\beta\gamma$ -dimethylethythrene in presence of foreign ethylenes yields always the

ordinary α - or α' -modification, mixed or "combined" forms not being obtained in this case.

The α -form of $\beta\gamma$ -dimethylerythrene caoutchouc, obtained at any temperature from 40° to 170° , and especially rapidly in the presence of a small proportion (1%) of piperidine piperidylthiocarbamate, belongs to the abnormal series, its elasticity point being 125 — 130° and its fatal temperature -5° . When vulcanised it acquires all the elastic properties of natural caoutchouc at 100° . T. H. P.

Preparation of Substances Equivalent to Ebonite, Celluloid, or Guttapercha. Synthesis of Vulcanised Caoutchouc. I. OSTROMISLENSKI (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1114—1131).—When treated with free chlorine, either natural or synthetic caoutchouc is converted into a substance which exhibits the properties of ebonite, in some cases to an enhanced degree. In its stability towards alkali or high temperatures it is the equal of ebonite, and, unlike the latter, it is very stable towards acids. Thus, the product obtained by the action of chlorine on synthetic normal erythrene caoutchouc is not changed by the prolonged action of nitric acid (D 1.35), by boiling fuming hydrochloric acid (D 1.19), by boiling chromic acid, or by concentrated sulphuric acid. It may be worked and polished like the best ebonite obtained from caoutchouc and sulphur, and is equally plastic. Its specific gravity is almost equal to that of ebonite and it is a better electrical insulator, its conductivity approximating to that of the best types of glass and bakelite. Ordinarily it is black, but if prepared under certain special conditions it may be obtained almost white or even colourless and transparent, and it is easily coloured. An ebonite-like substance may also be obtained by heating caoutchouc chloride or bromide (A., 1916, i, 278) in an iron mould out of contact with air at the ordinary temperature employed in vulcanising caoutchouc, but the product yielded in this way is always more or less porous.

Caouprene chloride, readily obtainable either from ethyl alcohol and sodium chloride through mono- or di-chloroethane (this vol., i, 405), or from carbon, lime, and hydrochloric acid through calcium carbide, may be easily converted into a plastic mass equivalent in its properties to celluloid, guttapercha, or the best ebonite. When treated with a very small proportion of naphthalene or copper oleate, the chloride yields a highly coherent ebonite; with camphor, paraffin-wax, or hexachloroethane a product corresponding with celluloid is obtained, whilst with oils, such as paraffin oil, esters, tri-, tetra-, or penta-chloroethane or with a large excess of naphthalene, etc., a substance with all the properties of natural guttapercha is formed. This synthetic ebonite exhibits the mechanical properties of ordinary ebonite, and is furthermore non-inflammable and of high stability towards acids or an atmosphere of moist chlorine.

Analogous products are obtainable in a similar manner from the higher chloride of caoutchouc, $C_{40}H_{48}Cl_{32}$, or the homologous chloro-caouprene chloride.

Experimental details are given.

T. H. P.

Synthesis of the Symmetrical Chloride and of the Higher Chloride of Erythrene Caoutchouc. New Chlorides of Natural Isoprene and Erythrene Caoutchoucs. I.

OSTROMISLENSKI (*J. Russ. Phys. Chem. Soc.*, 1916, 46, 1132—1151). —It has been already shown that polymerised vinyl bromide represents the symmetrical bromide of erythrene caoutchouc (A., 1916, i, 273), and the natural supposition that caouprene chloride is the corresponding symmetrical chloride is now justified experimentally.

Baumann (A., 1872, 890) described caouprene chloride as a viscous, plastic, insoluble mass, but these properties are caused by admixtures of extraneous liquids, such as the higher chloro-derivatives of ethane, esters of the fatty acids, etc., the chemically pure chloride being a snow-white, amorphous mass readily reducible to a fine powder. Caouprene chloride is rapidly formed by the action of the light from a mercury quartz lamp on liquid vinyl chloride, and exists in a soluble α -modification, which swells in various media to a more or less mobile layer, and in a more stable, insoluble γ -form; the former is completely converted into the latter by prolonged heating at 30—40° or by the action of the light from a mercury lamp. The relation between the α - and γ -caouprene chlorides is undoubtedly analogous to that between the α - and α' -forms of $\beta\gamma$ -dimethylethyrene caoutchouc (this vol., i, 402). The asymmetric chlorides of erythrene caoutchouc, and natural caoutchouc also exist in two modifications, namely, a soluble α - and an insoluble γ -modification. The molecular weight of α -caouprene chloride, measured cryoscopically in ethylene bromide solution, is 1021, which corresponds with the molecule $(\text{CH}_2\cdot\text{CHCl})_{16} = 999$; this result is in agreement with that obtained for caouprene bromide.

When heated with one of a number of different compounds, α - and γ -caouprene chlorides give ebonite-like substances which are identical with those obtained under analogous conditions from the asymmetric chloride of erythrene caoutchouc, and in their physical and mechanical properties closely resemble the ebonites obtained from the chloride of natural Para caoutchouc.

Like the bromide, caouprene chloride is a unicyclic halogenide, the ring containing sixteen $-\text{CHCl}\cdot\text{CH}_2-$ groups. The absence of double linkings is shown by its behaviour towards various reagents, such as permanganate, tetranitromethane, etc., and especially by its stability towards oxidising agents, like chromic acid and concentrated nitric acid (D 1.35), by its passivity towards halogen hydracids, including boiling hydrochloric acid, and towards concentrated sulphuric acid, and by the ability of the halogen present to react.

Unlike all natural and synthetic caoutchoucs and all their known halogenated derivatives, which are absolutely insoluble in acetone, α -caouprene chloride dissolves readily in this solvent. Gradual addition of a solution of the calculated amount of chlorine in carbon tetrachloride to a solution of erythrene caoutchouc in the same solvent yields an asymmetric chloride of erythrene caoutchouc, $\text{C}_{32}\text{H}_{48}\text{Cl}_{16}$, isomeric with caouprene chloride, from which it

differs only in the positions of the halogen atoms; this chloride also dissolves readily in acetone. Under the same conditions, natural caoutchouc gives a chloride of normal composition, $C_{32}H_{40}Me_8Cl_{16}$, also readily soluble in acetone. Like caouprene chloride, each of these chlorides exists in α - and γ -modifications. Owing to the solubility of the chlorides in acetone, they may be freed from admixtures of free caoutchouc and of colloidal higher chloride, and thus obtained in a chemically pure condition.

The polymeride of dichloroethylene yields a peculiar ebonite and is termed, by analogy, chlorocaouprene chloride. It is isomeric with the higher chloride of erythrene caoutchouc, obtained by the action of chlorine on a solution of the free caoutchouc, the isomerism depending on the position of the halogen. Under the influence of the active light of a quartz mercury lamp, *as*-dichloroethylene polymerises almost instantly.

Caouprene chloride has been prepared from ethyl alcohol and chlorine by the following reactions: (1) $EtOH = C_2H_4 + H_2O$, (2) $C_2H_4 + Cl_2 = C_2H_4Cl_2$, (3) $C_2H_4Cl_2 + NaOH = NaCl + H_2O + CH_2:CHCl$, and (4) $16CH_2:CHCl = (CH_2:CHCl)_{16}$. Owing to the "poisoning" of the alumina used as catalyst in the catalytic dehydration of alcohol, the yield of ethylene obtained gradually falls. It is found that this alumina may be regenerated by cautious ignition in a current of air and subsequent treatment with superheated steam. The yield of ebonite obtained amounts to at least 60 to 75 parts per 100 parts of absolute alcohol, and this is probably capable of considerable increase by varying the experimental conditions employed. Pure vinyl chloride has b. p. -12° , and not -18° as stated in the literature.

The asymmetric chloride of erythrene caoutchouc, $C_{32}H_{48}Cl_{16}$ (vide supra), is a snow-white, amorphous mass, which is readily powdered and becomes electrified when sieved through silk; it cannot be distinguished from caouprene chloride. It behaves towards permanganate like a saturated compound, remains colourless when treated with tetranitromethane, reacts with phenol, losing hydrogen chloride, and is passive towards nitric acid (D 1.35), concentrated sulphuric acid, boiling fuming hydrochloric acid (D 1.19), and boiling chromic acid. Under similar conditions, this chloride and caouprene chloride yield one and the same ebonite or one and the same plastic mass resembling celluloid or gutta-percha; the two substances behave similarly towards camphor, naphthalene, copper oleate, etc., and are soluble in the same solvents.

The chloride of natural Para caoutchouc cannot be distinguished from that of synthetic normal γ -isoprene caoutchouc, although they undoubtedly differ in the positions of the methyl groups in the nucleus. They are almost white, amorphous substances, which become electrified when rubbed, and, when pure, are easily powdered. Chemically and physically they behave like homologues of the chlorides of erythrene caoutchouc.

When treated in light petroleum (b. p. up to 80°) solution with

a current of anhydrous chloride at 0° , α -erythrene caoutchouc yields a higher chloride, $C_{82}H_{32}Cl_{32}$, which is white, amorphous, and opaque, and may be readily crushed. T. H. P.

Catalytic Acceleration of the Vulcanising Process. S. J. PEACHEY (*J. Soc. Chem. Ind.*, 1917, **36**, 424—429).—An account is given of the earlier history of vulcanisation and of the use of mineral accelerators. The first powerful organic accelerator to be used appears to be piperidine (Bayer & Co., D.R.-P., 265221, 1912); subsequently the use of all organic bases possessing a dissociation constant greater than 1×10^{-8} has been patented by the same firm (D.R.-P., 280198, 1914).

The author has found that the nitroso-derivatives of certain bases, such as dimethylaniline, methylaniline, and diphenylamine, are capable of acting as powerful accelerators of the vulcanising process (Brit. Pat., 4263, 1914). Generally speaking, the addition of 0.3 to 0.5% of nitroso-base to any mixing of good quality is sufficient to reduce the time of vulcanisation to from one-quarter to one-third of that normally required. In the case of red mixings containing antimony sulphide as the vulcanising agent and no added sulphur, the accelerator fails to develop its full effect. In such cases it becomes necessary to introduce a certain amount of sulphur and to employ the sulphide mainly as a pigment. The presence of litharge in any quantity tends to diminish the effectiveness of the organic accelerator whilst, on the other hand, magnesia in small amounts very considerably augments the accelerating power of the nitroso-base. The maximum accelerating power of *p*-nitrosodimethylaniline is only fully manifested when new rubber is used.

The action of organic accelerators appears to be entirely catalytic in its nature.

It may be noted that whilst the nitroso-derivatives of such bases as methylaniline, ethylaniline, diphenylamine, and others are powerful accelerators, the isomeric nitrosoamines have not a similar effect.

The catalytic action of the nitroso-bases appears to depend on the presence of the nitroso-group, and not on their basic nature; it is also shown by certain nitroso-compounds, which are quite destitute of basic properties, for example, nitrosophenol and nitrosonaphthol.

It has further been found that the condensation products formed by the action of amines on aldehydes, for example, benzylidene-ethylamine, benzylideneaniline, and hydrobenzamide (Brit. Pat., 7370, 1914), have a marked effect in accelerating the vulcanisation of rubber, but they are considerably less effective than the nitroso-compounds.

It is interesting to note that certain substances, such as phenylhydrazine, have an anti-catalytic action on the vulcanisation of rubber.

H. W.

The Constitution of Amygdalin. ARMINIUS BAU (*Biochem. Zeitsch.*, 1917, **80**, 159—162).—*Saccharomycodes Ludwigii* (Hansen) contains amygdalase as well as yeast emulsin, but no maltase. The facts confirm the views expressed by Auld, Caldwell, and Courtauld that the disaccharide of amygdalin, $C_{12}H_{22}O_{11}$, is not maltose, although it undergoes scission into two molecules of dextrose.

S. B. S.

Chemical Constitution of Chitin. S. MORGULIS (*Science*, 1916, **44**, 866—867; from *Physiol. Abstr.*, 1917, **2**, 103).—In the hydrolysis of chitin (from lobsters) by sulphuric acid very little volatile acid is formed at first, although all the dextrose molecules may have been split off. A large amount of volatile acid is formed when the sugar itself is attacked by the acid. In addition to acetic, some formic acid is formed (up to 2%) and probably also other volatile acids. The maximum yield of sugar is 81%. The amino-group is readily eliminated from the glucosamine as ammonium sulphate. The amino-nitrogen represents only seven-eighths of the total nitrogen, the more resistant remaining nitrogen fraction being obtained by digestion with concentrated sulphuric acid; the relation between the two kinds of nitrogen is remarkably constant. These results do not confirm the prevalent idea that chitin is a polymerised acetylglucosamine. The molecule apparently consists of two parts, one containing all the dextrose and all the amino-groups, the other being a stable nitrogen compound not yielding dextrose. The acetic acid is not a primary fission product, but a secondary product of the hydrolysis, and the same is true of monoacetylglucosamine or monoacetyldiglucoamine.

G. B.

Solanine. A. HEIDUSCHKA and H. SIEGER (*Arch. Pharm.*, 1917, **255**, 18—44).—An examination of solanine obtained from potato shoots.

On account of the tendency of solanine to decomposition and to sublimation, the m. p. of the substance is rather indefinite; a more valuable characteristic is the optical activity in 2% hydrochloric acid, $[\alpha]_D^{20} -42.16^\circ$.

The composition of the pure substance obtained in the present investigation was different from that given by earlier workers, and agreed best with a formula $C_{52}H_{91}O_{18}N$. Contrary to previous statements (Zwenger and Kind, *Annalen*, 1859, **109**, 244), the hydrochloride ($C_{52}H_{91}O_{18}N.HCl$) was obtainable in a crystalline condition, m. p. 212° (decomp.), after sintering at 177° , but no oxalate could be isolated.

Hydrolysis of solanine is best effected with 2% hydrochloric acid solution; the resulting solanidine, m. p. 207° , judged by its composition and molecular weight in phenol, possesses the formula $C_{34}H_{57}O_2N$. The hydrolytic fission of solanine is not complete, but, by allowing for the unaltered solanine, and measuring the extent to which the resulting sugars affect Fehling's solution, it is calculated that each molecule of solanine gives one molecule each of solanidine, dextrose, galactose, and rhamnose.

Heating with ethyl iodide in alcoholic solution failed to effect the introduction of the ethyl radicle, and attempts at acetylation failed to give any definite product (compare Hilger, A., 1879, 541). The dehydration of solanidine by concentrated hydrochloric acid or other agents yielded not only solanicine, $C_{34}H_{55}ON$, but also a base intermediate between this and solanidine probably derived from solanidine by the elimination of a semi-molecular proportion of water.

Solanine was also found to form an additive compound with phytosterol, and also, when heated, to evolve vapours which redden a pine shaving.

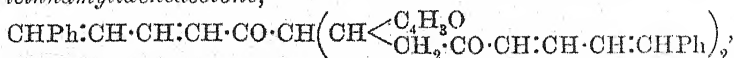
An examination of solanine from the *Palo Natri* of Chile showed this substance to be identical with the product from potatoes.

D. F. T.

Bixin. A. HEIDUSCHKA and A. PANZER (*Ber.*, 1917, 50, 546—554).—The empirical formulæ assigned to bixin by van Hasselt, Heiduschka, and Riffart, and Herzig and Faltis seem to depend on the method by which the pigment is purified. Analyses based on various methods of isolation and crystallisation are now discussed, but it appears that most dependence is to be placed on a specimen which has been purified by acetone in the usual way and then crystallised from ethyl acetate. The analysis and methoxyl and molecular-weight determinations of such a product agree with the formula $C_{25}H_{30}O_4$, which was obtained by Pregl on behalf of Herzig and Faltis (A., 1915, i, 572).

J. C. W.

Action of Furfuraldehyde on Cinnamylidenemethyl Methyl Ketone. M. GIUA (*Gazzetta*, 1917, 47, i, 86—89).—By the condensation of furfuraldehyde (1 mol.) with cinnamylidenemethyl methyl ketone (1 mol.) in presence of sodium hydroxide, Bauer and Dieterle (A., 1911, i, 921) obtained β -styryl β' -furyldivinyl ketone. The author finds that this condensation yields also *difurfurylidene-tricinnamylideneacetone*,



which forms golden-yellow crystals, m. p. 215—216°, gives a brick-red coloration with concentrated sulphuric acid, and may also be obtained by polymerisation of β -styryl β' -furyldivinyl ketone in benzene solution in sunlight; indications of the existence of a second stereoisomeride were obtained (compare v. Kostanecki and Roszbach, A., 1896, i, 551; v. Kostanecki and Podrajansky, A., 1896, i, 689).

T. H. P.

Bromine Substitution Products of Chromones [Benzopyrones]. H. SIMONIS and L. HEROVICI (*Ber.*, 1917, 50, 646—652).—The bromination of 2:3-dimethylchromone is described (compare A., 1913, i, 890). In the cold, this compound merely absorbs bromine at the ethylene linking, but the halogen atoms are given up again when the product is dried. Under more strenuous conditions, the methyl groups are attacked, but the benzene nucleus is

only affected in extreme cases, which is proved by the fact that the simpler bromo-derivatives yield unsubstituted salicylic acid on hydrolysis.

With bromine in boiling benzene the products are *ω*-bromo-2:3-dimethyl- γ -benzopyrone, $C_6H_4 \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ O \end{smallmatrix} C_2Me \cdot CH_2Br$, m. p. 171—172°, and *ωω*-dibromo-2:3-dimethylbenzopyrone, prisms, m. p. 193°, which is the less soluble in ether of the two. Except that the bromine atoms are in the side-chains, no more can be said as yet with regard to their positions relative to the pyrone ring. The monobromide may be hydrolysed by alcoholic silver nitrate to an oily *hydroxy*-compound. Bromination in carbon disulphide solution under pressure at 140° gives rise to the same products unless at least four molecular proportions of bromine and a little iodine are used, when a *tetrabromo*-compound, rhombic plates, m. p. 215°, and two less soluble *tribromo*-derivatives, prisms, m. p. 168°, and stellate groups of needles, m. p. 185°, are formed. There are indications of the presence of the $-CHBr_2$ group and of bromine in the benzene nucleus in these compounds. J. C. W.

Scopoline Bromide. ERNST SCHMIDT (*Arch. Pharm.*, 1917, 255, 72—75. Compare A., 1916, i, 285, 419).—For a final decision as to the constitution of scopoline it is necessary to ascertain the nature of the oxygen atom adjacent to the hydroxyl radicle. From the chemical inactivity of this oxygen atom it appears probable that an ether grouping is present, but in order to avoid the possibility that the inertness of this oxygen atom may be due to the proximity of the hydroxyl group, the author has prepared *scopoline bromide*, $C_{18}H_{19}ONBr$ (*hydrobromide*, prisms, m. p. 226—227° decomp.; *aureichloride*, pale red cubes, m. p. 211° decomp.; *platini-chloride*, brownish-red prisms or needles, m. p. 221—222°), by the action of phosphorus pentabromide on scopoline hydrobromide.

In this compound the hydroxyl group of scopoline has been replaced by a bromine atom, and the chemical behaviour of the remaining oxygen atom is to be examined further. D. F. T.

Alkaloids of Ipecacuanha Root, Uragoga Ipecacuanha. III. OSKAR KELLER (*Arch. Pharm.*, 1917, 255, 75—80. Compare A., 1914, i, 428; 1911, i, 1014).—The paper consists of a commentary on the results of the author in comparison with those of Hesse (A., 1914, i, 722), Carr and Pyman (T., 1914, 105, 1591), Hermanns (*Diss.*, Freiburg, 1915), Karrer (A., 1916, i, 833), and Paul and Cownley (A., 1894, i, 155). D. F. T.

The Alkaloids of Ipecacuanha. II. P. KARRER (*Ber.*, 1917, 50, 582—586. Compare A., 1916, i, 833).—Karrer finds that his oxidation product, “dehydroemetine,” is identical with Carr and Pyman’s “rubremetine” [as Pyman has also suggested in the meantime; see T., 1917, 111, 423].

Carr and Pyman experienced a difficulty in the reduction of dehydroemetine (rubremetine), but it is now found that the iodide

is readily reduced to an isomeride of emetine by the gradual addition of zinc dust to a boiling solution in a mixture of dilute acetic and sulphuric acids. *isoEmetine* is an amorphous substance, m. p. 50—55°, which couples with diazotised sulphanilic acid even in neutral solution, giving a product which becomes deep bluish-violet with acids and is thus distinguished from emetine. The *hydrobromide* and *hydriodide*, B_2HX , and the *dimethiodide* of *N-methylisocemetine*, $C_{20}H_{30}O_4N_2Me_2 \cdot 2MeI$, m. p. 185—195°, have been prepared.

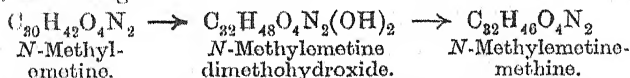
J. C. W.

Alkaloids of Ipecacuanha. II. FRANK LEE PYMAN (T., 1917, 111, 419—446. Compare T., 1914, 105, 1591).—In extension of the earlier work, two new alkaloids of ipecacuanha have been examined and *N-methylemetine* investigated more fully.

The non-phenolic, ether-soluble alkaloids are converted into the hydrobromides and the aqueous mother liquor left after crystallising the emetine salt is so treated that the hydrogen oxalates of the minor bases are isolated. The mixture is basified and the alkaloids separated by fractional extraction with acids from the chloroform solution. The more basic alkaloid, amounting to 0.015 to 0.033% of ipecacuanha, is shown to be identical with the *O-methyl ether* of *psychotrine*. This yields emetine and *isoemetine* on reduction (and another base, designated "C"), just as *psychotrine* yields *cephaeline* and *isocephaeline*. Conversely, when emetine is oxidised with two atomic proportions of iodine, it yields *methylpsychotrine*, and both these further give *rubremetine* on oxidation with more iodine or bromine. *Methylpsychotrine* forms an *N-benzoyl* derivative, and therefore these bases are secondary.

The less basic alkaloid amounts to about 0.002—0.006% of ipecacuanha. It is designated *emetamine* and probably contains a $-C:C-$ and a $-C:N-$ linking.

N-Methylemetine salts are described, and its degradation to a methine, according to the scheme:



For the detailed account of the many new salts and derivatives the original must be consulted.

J. C. W.

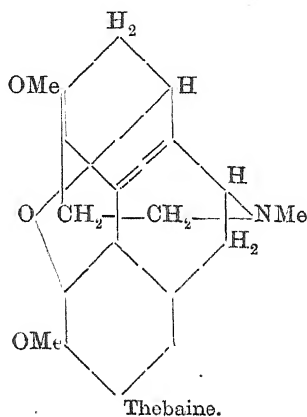
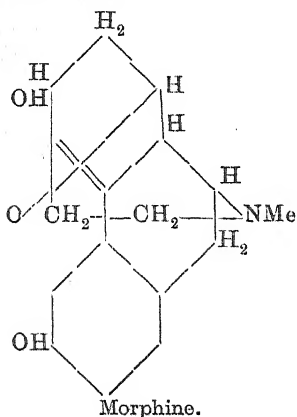
Cephaeline Butyl Ether and Salts thereof. J. W. MEADER (Brit. Pat., 104652; addition to Brit. Pat., 11717; from *J. Soc. Chem. Ind.*, 1917, 36, 520).—*Cephaeline butyl ether* [as distinguished from the *isobutyl* ether claimed in the principal patent (this vol., i, 91)] is prepared by the action of an alkali metal and a butyl haloid on *cephaeline*. The details of the preparation and the properties of the product are the same as for the *isobutyl* ether.

H. W.

Preparation of Cephaeline Allyl Ether. ELI LILLY & Co. (U.S. Pat., 1209575; from *J. Soc. Chem. Ind.*, 1917, 36, 520).—*Cephaeline allyl ether*, $C_{28}H_{37}O_3N_2 \cdot O \cdot C_3H_5$, is prepared by treating *cephaeline* with sodium ethoxide and allyl bromide.

H. W.

Constitution of Morphine. FRANZ FALTIS (*Arch. Pharm.*, 1917, 255, 85—112).—A critical review of most of the work on morphine and its related bases accomplished by Vongerichten, Knorr, Freund, and von Braun during the last ten years or so. It is shown that the conflicting results can be explained on the basis of the annexed formulæ for morphine and thebaine, in which the oxide ring is different from that in Knorr's formula and is under considerable tension.



J. C. W.

An Anomaly in the Solubility of Sparteine. AMAND VALEUR (*Compt. rend.*, 1917, 164, 818—820).—A saturated aqueous solution of sparteine becomes turbid with a very slight rise in temperature, but if the solution is diluted, a greater rise in temperature is necessary to produce turbidity. This phenomenon is exhibited by all solutions down to a dilution of 0.14 gram per 100 c.c. In the presence of sodium carbonate, much more dilute solutions become turbid. The values of the temperature at which turbidity occurs for various dilutions of sparteine in the presence of 5% aqueous sodium carbonate are given, and a method for the estimation of sparteine based on these data is described.

W. G.

Condensation of Pyrrole with Methyl Ethyl Ketone, Methyl Hexyl Ketone, and with Acetone and Methyl Ethyl Ketone together; its Bearing on the Formulæ for Chlorophyll and Hæmin. V. V. TSCHELINEV and B. V. TRONOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1197—1209. Compare this vol., i, 91, 93, 164).—The condensation of pyrrole with methyl ethyl ketone under the conditions previously employed yields: (1) a crystalline compound, $C_{32}H_{44}N_4$, m. p. 149.5—150.5°, having in freezing benzene the molecular weight corresponding with the above formula, and (2) a small proportion of a crystalline isomeride, m. p. 162°, having the correct molecular weight in freezing benzene. These compounds evidently contain four pyrrole

residues and four ketone residues in the molecule, and the pyrrole residues are regarded as connected in the 2- and 5-positions by way of the carbonylic carbons of the ketone residues (*loc. cit.*); if the methyl and ethyl groups of the ketone are able to occupy different positions, so as to give rise to cis-trans isomerism, four isomerides should be possible.

The above reaction was investigated by Dennstedt and Zimmermann (A., 1887, 598, 1052), who attributed to the resultant products the formulæ $(C_{16}H_{22}N_2)_3 \cdot 5H_2O$ and $(C_{16}H_{22}N_2)_3 \cdot H_2O$. The authors show that such compounds do not exist, but that it is possible, on crystallisation from alcohol, to obtain an unstable compound, $C_{32}H_{44}N_4 \cdot 2EtOH$, initial m. p. about 80° , which readily loses alcohol, and thus becomes converted into the compound, m. p. $149.5-150.5^\circ$. Dennstedt and Zimmermann's compound, $(C_{16}H_{22}N_2)_3 \cdot 5H_2O$, is regarded as $C_{32}H_{44}N_4 \cdot 2MeOH$.

Similar condensation of pyrrole with methyl hexyl ketone results in a small yield of a colourless, crystalline compound, $C_{48}H_{76}N_4$, m. p. 179° , which gives the normal molecular weight in freezing benzene. The principal product of the reaction is a viscous oil, which possibly contains others of the possible isomerides.

Condensation of pyrrole with acetone and methyl ethyl ketone simultaneously yields the crystalline compound, $C_{30}H_{40}N_4$, m. p. $203-204^\circ$, which exhibits the normal molecular weight in freezing benzene. The molecule of this compound evidently contains four pyrrole residues, two acetone residues, and two methyl ethyl ketone residues.

Constitutions are proposed for these products similar to that already suggested for the tetrapyrrole-tetra-acetone compound (*loc. cit.*), and it is shown that in the compounds obtained from methyl ethyl ketone, and from this together with acetone, the four iminic hydrogen atoms of the pyrrole residues in the molecule remain unreplaced.

T. H. P.

Condensation of Pyrrole with *cyclo*Hexanone, other Cyclic Ketones, and Acetone and *cyclo*Hexanone together. Capacity of different Ketones for Condensation with Pyrrole. V. V. TSHELINCEV, B. V. TRONOV, and S. G. KARMANOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1210-1221).—The condensation of pyrrole with benzophenone (compare Tschelincev, Tronov, and Terentéev, A., 1915, i, 990) yields a product representing only the first stage of the condensation, in which for two molecules of pyrrole there is only one molecule of benzophenone, whereas when aliphatic ketones are used, more advanced condensation takes place. With the hope of obtaining intermediate products capable of throwing light on these condensations, the authors have made experiments with various cyclic ketones.

With *cyclo*hexanone, pyrrole yields the compound, $C_{20}H_{26}N_2$, which crystallises in slender needles, m. p. 272° , and has the normal molecular weight in freezing benzene. This compound is therefore simpler than those obtained with aliphatic ketones, as it contains only two ketonic residues and two pyrrole residues;

the two iminic hydrogen atoms in the latter are unsubstituted. With acetyl chloride at the ordinary temperature, it gives a deep red, solid product similar to that formed by the acetone condensation product, and with silver nitrate in alcoholic solution it yields the double compound, $C_{20}H_{26}N_2 \cdot AgNO_3$, as a white precipitate (compare Dennstedt and Zimmermann, A., 1887, 598, 1052).

With each of the three ketones, menthone, fenchone, and camphor, pyrrole is capable of condensing with greater or less rapidity, but the products obtained were oily or amorphous, and no pure individuals could be isolated.

When condensed with acetone and cyclohexanone together, pyrrole yields: (1) the compound, m. p. 272° , obtained with cyclohexanone alone; (2) the tetrapyrrole-tetra-acetone compound, m. p. 296° (compare this vol., i, 91); and (3) a compound, $C_{34}H_{44}N_4$, which forms crystals, m. p. $218-220^\circ$, and has the normal molecular weight in freezing benzene. This compound contains two cyclohexanone residues, two acetone residues, and four pyrrole residues, but only two iminic hydrogens remain free; a structural formula in agreement with these facts is proposed.

The yields of condensation products formed by pyrrole with different ketones are as follows: with acetone, 93.5%; cyclohexanone, 59%; methyl ethyl ketone, 54%; methyl hexyl ketone, 7%; and benzophenone, 3%. With the exception of cyclohexanone, for which data are lacking, the above order is that of the higher atomicities of the oxygen atoms of these ketones, as measured by the thermal effects of their action on organo-magnesium alkyl-oxides.

T. H. P.

Nitrosopyrrole-black. A. ANGELI and GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1917, [v], 26, i, 273—278. Compare A., 1915, i, 912, 918, 1025).—When an aqueous solution of the sodium salt of isonitrosopyrrole is treated with carbon dioxide, or when pyrrole reacts with ethyl nitrite or nitrous acid, a black powder, named *nitrosopyrrole-black*, is obtained. This product is almost insoluble in all solvents, but dissolves easily in alkali and is reprecipitated by acid; in alkaline solution it is instantly oxidised by permanganate and is decolorised by reducing agents, the dark colour subsequently reappearing in the air. The composition agrees approximately with the formula $(C_4H_3ON_2)_n$. Nitrosopyrrole-black does not melt, but at a high temperature deflagrates with liberation of red vapours.

This compound appears to be accompanied by another, also black, which has not yet been investigated.

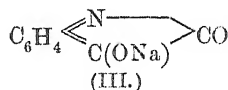
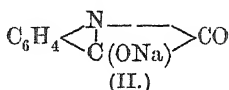
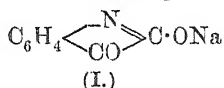
In nitrosopyrrole-black the CO-group of pyrrole-black is replaced by $NO:(C_4N)CO \rightarrow (C_4N)NO$.

T. H. P.

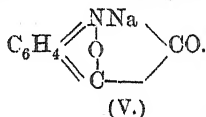
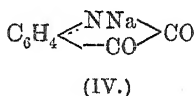
Constitution of the Blue Isatin Salts. M. CLAASZ (*Ber.*, 1917, 50, 511—515).—In his discussion on the constitution of the salts of isatin and its derivatives, Heller declared that the different colours of the salts were due to the different attachments of the metal, the *N*-salts being deeper in colour than the *O*-salts, and he

suggested that this kind of isomerism should be taken into account in other cases (this vol., i, 219). It is now stated that the question can be very easily solved by taking cognisance of the stability of the salts towards water, for no cases of *N*- or *C*-metallic salts are known which are stable towards water. Isatin gives a blue salt which is soluble in water and therefore can only be an *O*-salt. Heller furthermore criticised as unnecessary Claasz's new betaine-like formula for indigoid substances (A., 1916, i, 839), but this actually helps to explain the relationships in the case of isatin, whereas Heller's theory is untenable.

Isatin can give three *O*-salts, thus:



Of these, salt II is the red salt of the red isomeride of isatin, namely, isatol, the discovery of which by Heller is a real contribution to the difficult problem. The blue salt, III, is soluble in water and owes its enhanced colour to the multiplication of chromophores; it is quinonoid. The deep blue *N*-sodium salt of isatin changes to red with water, owing to conversion into an *O*-salt. Its colour cannot be due only to the attachment of the metal, as there is a blue *O*-salt as well; neither can Heller's formula, IV, explain it, for this contains no chromophores. The "internal-salt" formula, V, containing Claasz's indigo chromophore, is more plausible:

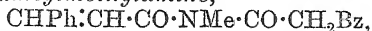


J. C. W.

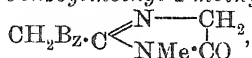
Intramolecular Rearrangements and Ring Closures with Derivatives of Benzoylacetamide. ANDREAS KNUST and OTTO MUMM (*Ber.*, 1917, 50, 563—574).—In an earlier paper (A., 1915, i, 244) it was shown that diacylamines can sometimes exist or behave in the unusual, but possible, form, $\text{R} \cdot \text{C}(\text{:NH}) \cdot \text{O} \cdot \text{CO} \cdot \text{R}'$. Compounds of this type can, of course, be prepared by the interaction of the sodium salt of an acid with an imide chloride, but it is not easy to say whether this structure is retained or whether rearrangement into the true diacylamine, $\text{R} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{R}'$, takes place unless the product is capable of some indicative change. The most promising imide chlorides and acids to work with are those that offer opportunities for intramolecular ring closures, and the investigation already opened has now been advanced considerably in this direction. The methosulphate of 5-phenylisooxazole is readily obtainable, and is known to react with the salts of organic acids as though it were benzoylacetmethylimide sulphate, $\text{COPh} \cdot \text{CH}_2 \cdot \text{C}(\frac{1}{3}\text{SO}_4) \cdot \text{NMe}$, that is, as a compound containing a reactive methylene and a ketone group. This agent has therefore been used extensively in the present investigation.

A concentrated aqueous solution of the agent reacts with sodium

pyruvate to form *benzoylmethylmaleimethylimide* [2:5-diketo-4-benzoyl-1:3-dimethyl-2:5-dihydropyrrole], $\text{NMe} \begin{smallmatrix} \text{CO} \cdot \text{CBz} \\ | \\ \text{CO} \cdot \text{CMe} \end{smallmatrix}$, which crystallises in slender needles, m. p. 247°. Sodium cinnamate yields *benzoylacetylcinnamoylmethylamine*,



m. p. 97°, which gives the methylamide of cinnamic acid, m. p. 111°, on boiling with dilute alcoholic hydrochloric acid. Sodium aminoacetate yields *2-benzoylmethyl-1-methylglyoxalone*,



m. p. 219°, which has acidic properties. Sodium malonate forms β -*phenylglutaconmethylimide* (2:6-diketo-4-phenyl-1-methyl-1:2:3:6-tetrahydropyridine) in yellowish-brown crystals, m. p. 164°. This can be titrated as an acid, but it also forms an unstable *hydrochloride*, m. p. 204°, and *sulphate*, m. p. 256°.

In all these cases, therefore, the original *O*-acyl derivative has only a transitory existence. The isolated compounds are the products of subsequent ring closures of the diacylamines.

The above reagent also combines with phenol in a strong solution of sodium hydrogen carbonate, giving *phenyl methyliminobenzoylacetate*, $\text{CH}_2\text{Bz} \cdot \text{C}(\text{NMe}) \cdot \text{OPh}$, in white, rhombic crystals, m. p. 100°. This ester cannot be rearranged into methylbenzoylacetyl-anilide, but it readily yields phenol on boiling with alcoholic hydrochloric acid.

With potassium cyanate, the product is *4-amino-5-benzoyl-1-methyluracil*, $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{CBz} \cdot \text{CO} \\ | \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{NMe}$, which forms unstable salts with acids (*acetate*, white needles, m. p. 302°; *hydrochloride*, leaflets; *nitrate*, large octahedra), and also yields a *potassium salt* and is converted into the 1:3-dimethyl compound, broad needles, m. p. 250°, by means of methyl sulphate. The mother liquor from the crystallisation of the product from glacial acetic acid contains a small quantity of *4-phenyl-1-methyluracil*, which separates from alcohol in stout, rhombic crystals, m. p. 221°, forms a *hydrochloride* with the same m. p., but does not dissolve in sodium hydroxide.

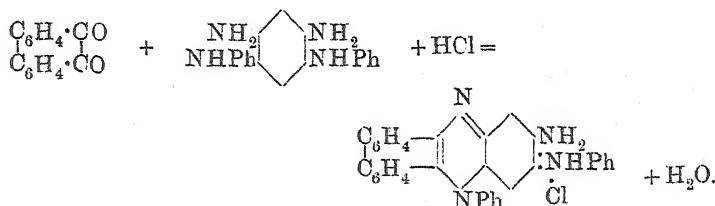
Ethyl sodiomalonate yields the enolic form of *ethyl methyliminobenzoylacetylmalonate*, $\text{OH} \cdot \text{CPh} \cdot \text{CH} \cdot \text{C}(\text{NMe}) \cdot \text{CH}(\text{CO}_2\text{Et})_2$, in long needles, m. p. 121°, which is hydrolysed and condensed by boiling with alcoholic potassium hydroxide to *4-methylamino-6-phenyl-1:2-pyrone-3-carboxylic acid*, $\text{NHMe} \cdot \text{C} \begin{smallmatrix} \text{CH} = \text{CPh} \\ | \\ \text{C}(\text{CO}_2\text{H}) \cdot \text{CO} \end{smallmatrix} \text{O}$, m. p. 201°, and this loses carbon dioxide when heated at 205°, forming *4-methylamino-6-phenyl-1:2-pyrone*, m. p. 180° (*hydrochloride*, m. p. 117°). Ethyl sodioacetoacetate yields *4-methylamino-3-acetyl-6-phenyl-1:2-pyrone*, in rhombic leaflets, m. p. 161°, which are quite neutral.

J. C. W.

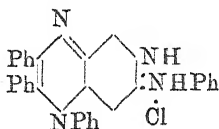
Azine Dyes. F. KEHRMANN (*Ber.*, 1917, 50, 554—563).—[With RENÉ SPEITEL].—*Phenylaposafranine*.—This dye is most conveniently prepared by eliminating the amino-group in ψ -mau-

veine through the diazo-reaction, the latter compound being obtained by oxidising a mixture of *p*-phenylenediamine and diphenyl-*m*-phenylenediamine. The nitrate (annexed formula) crystallises in very long, brassy needles. When boiled with aniline and aniline hydrochloride, phenylaposafranine yields the insoluble chloride of 2:3-dianilino-10-phenylphenazine and a small quantity of the soluble, blue chloride of 2:8-dianilino-10-phenylphenazine (diphenylphenosafranine. Compare A., 1898, i, 153).

[With MAX WEILENMANN.]—*Constitution of the Anilino-derivative of 2-Aminoflavinduline.*—When 2-aminoflavinduline chloride is treated with aniline it yields the chloride of 2-amino-3-anilino-flavinduline (A., 1900, i, 255). The proof for this constitution is that the dye can be obtained by condensing phenanthraquinone with 4:6-dianilino-*m*-phenylenediamine, thus:



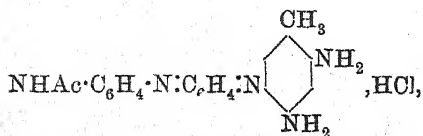
A similar condensation has been effected with benzil.



The *product* (annexed formula) crystallises in metallic-green needles; the free base forms green leaflets, m. p. 235°; the *nitrate* forms brassy needles; the *platinichloride* is an almost insoluble, dark red, bronzy powder, and the *dichromate* is an insoluble, reddish-brown powder.

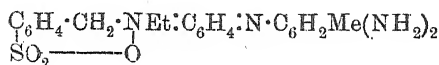
[With WLADISLAUS POPLAWSKI.]—*Some New Indamines.*—It was hoped that by introducing aryl groups into the amino-group of an indamine, some improvement in the tinctorial value of these compounds might be effected. Some new indamines of the type of tolylene-blue have accordingly been prepared, using nitroso-derivatives of diphenylamines instead of the usual dimethylaniline, but the dyes are not sufficiently fast to acids or light to make them of any real value.

p-Nitroso-*p*-acetylaminodiphenylamine, glistening, reddish-brown needles, m. p. 218° (decomp.), yields with *m*-tolylenediamine a

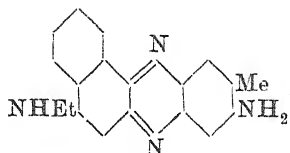


the annexed formula when the alcoholic solutions are warmed at 30° for some time with a little acetic acid, whilst at 60° the *p*-acetyl-amino-group is re-

placed by hydrogen and a similar blue *indamine* is formed. *p*-Nitrosoethyl-*p*-sulphobenzylaniline yields an *indamine* of the formula A, whilst nitrosoethyl- α -naphthylamine does not form an *indamine*, but the corresponding metallic-green *hydrochloride* of the *azine*, B:

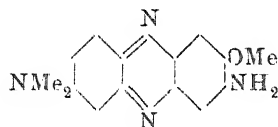


A.



B.

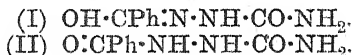
6-Methoxy-*m*-phenylenediamine (2:4-diaminoanisole) reacts



with *p*-nitroso-*p'*-acetylaminodiphenylamine to form a violet-blue *indamine*, $\text{C}_{21}\text{H}_{21}\text{O}_2\text{N}_5 \cdot \text{HCl}$, and with *p*-nitrosodimethylaniline to form the brownish-red *azine*, m. p. 258° , of the annexed formula. This can be methylated by means of methyl sulphate, and the product forms a *platinichloride*, $\text{C}_{32}\text{H}_{36}\text{O}_2\text{N}_8 \cdot \text{H}_2\text{PtCl}_6$. J. C. W.

Acylsemicarbazides and Acylsemicarbazic Acids.

J. BOUGAULT (*Compt. rend.*, 1917, 164, 820—822).—A comparison of the benzoylsemicarbazide prepared from phenylglyoxylic acid (compare A., 1916, i, 764, 765) with that obtained by Widman and Cleve (compare A., 1898, i, 335) from benzoic anhydride and semicarbazide. The latter compound is acidic in character and is considered to be the isomeride (I), whilst the semicarbazide obtained from phenylglyoxylic acid is considered to be the isomeride (II).



Compounds of the type I, which are acidic, are obtained by the action of semicarbazide on acid anhydrides or chlorides, and for these the author suggests the name acylsemicarbazic acids, to distinguish them from compounds of the type II, which are basic and can only be obtained by the action of iodine and sodium carbonate on the semicarbazones of α -ketonic acids. W. G.

Oxidation of Phenylazocarbonamide. A. ANGELI (*Atti R. Accad. Lincei*, 1917, [v], 26, i, 207—213).—The azoxy-compound obtained (this vol., i, 228) by oxidising phenylazocarbonamide by means of hydrogen peroxide yields nitrogen and phenol when boiled with 25% sulphuric acid solution, evidently by way of phenylazocarboxylic acid and benzenediazonium sulphate. It is highly sensitive to the action of alkali hydroxide or carbonate, addition of a few drops of sodium carbonate solution to a boiling aqueous solution containing the amide and β -naphthol resulting in the immediate appearance of the scarlet coloration characteristic of benzeneazo- β -naphthol.

Since phenylazoxycarbonamide remains unchanged when treated at the ordinary temperature with bromine in the absence of any solvent, its structure is regarded as represented by the formula $O:NPh:N\cdot CO\cdot NH_2$, and not by $NPh:NO\cdot CO\cdot NH_2$. It is isomeric with, but much more stable than, the nitrosoamine of phenylcarbimide, $NH_2\cdot CO\cdot NPh\cdot NO$, which yields nitrogen and phenol when boiled with water. On reduction, phenylazoxycarbonamide is converted into the original phenylazocarbonamide (compare Widman, A., 1895, i, 603). T. H. P.

***p*-, *o*- and *m*-Tolueneazo- α -naphthylhydrazinesulphonic Acids.** J. TRÖGER and G. LANGE (*Arch. Pharm.*, 1917, 255, 1—7).—It has already been shown that under suitable conditions benzene-diazonium salts can be converted into the corresponding hydrazinesulphonic acids by the action of sulphur dioxide on the aqueous solution, aminoazobenzene after diazotisation being convertible by this process into benzeneazophenylhydrazinesulphonic acid, $N_2Ph\cdot C_6H_4\cdot NH\cdot NH\cdot SO_3H$ (Tröger and Puttkamer, A., 1907, i, 263; Tröger and Westerkamp, A., 1910, i, 207), and the authors have now extended this reaction to the diazo-compounds derived from the tolueneazo- α -naphthylamines.

p-Tolueneazo- α -naphthylamine (Weselsky and Benedict, *Ber.*, 1879, 12, 229) when diazotised at 20° yields an insoluble, brown solid, together with the solution of the diazo-compound, the latter on addition to a solution of potassium sulphite and potassium carbonate undergoing conversion into potassium *p*-tolueneazo- α -naphthalenediazosulphonate, $C_6H_4Me\cdot N_2\cdot C_{10}H_6\cdot N_2\cdot SO_3H$; this separates in a labile, reddish-brown modification, which shortly becomes deep brown. When warmed with ammonium sulphide in aqueous solution, the potassium diazosulphonate is reduced to the potassium salt (brown needles) of *p*-tolueneazo- α -naphthylhydrazinesulphonic acid, $C_6H_4Me\cdot N_2\cdot C_{10}H_6\cdot NH\cdot NH\cdot SO_3H$, the free acid when dry forming a violet-black powder. This sulphonic acid when mixed with an aromatic aldehyde and a little alcoholic hydrogen chloride is capable of giving condensation products with elimination of the sulphonic acid group; by this reaction there were obtained *p*-tolueneazo- α -naphthylsalicylidenehydrazine,

$C_6H_4Me\cdot N_2\cdot C_{10}H_6\cdot NH\cdot N:CH\cdot C_6H_4\cdot OH$, deep red prisms, m. p. 166·5° (*hydrochloride*, deep green, crystalline powder); *p*-tolueneazo- α -naphthylcinnamylidenehydrazine, $C_6H_4Me\cdot N_2\cdot C_{10}H_6\cdot NH\cdot N:CH\cdot CH:CHPh$, deep reddish-brown prisms, m. p. 168·5° (*hydrochloride*, black powder with green lustre; *p*-tolueneazo- α -naphthylanisylidenehydrazine,

$C_6H_4Me\cdot N_2\cdot C_{10}H_6\cdot NH\cdot N:CH\cdot C_6H_4\cdot OMe$, brown crystals, m. p. 156° (*hydrochloride*, greenish-black crystals); *p*-tolueneazo- α -naphthyl-*p*-tolylidenehydrazine,

$C_6H_4Me\cdot N_2\cdot C_{10}H_6\cdot NH\cdot N:CH\cdot C_6H_4Me$, brownish-black prisms, m. p. 159° (*hydrochloride*, bluish-black crystals).

o-Tolueneazo- α -naphthylamine, $C_6H_4Me\cdot N_2\cdot C_{10}H_6\cdot NH_2$, red, silky needles, m. p. 99° (*hydrochloride*, bluish-violet needles;

sulphate, pale violet needles with $3\text{H}_2\text{O}$; *nitrate*, greenish-black crystals), prepared by the interaction of an aqueous diazotised solution of *o*-toluidine and alcoholic α -naphthylamine, was by the usual process of diazotisation and subsequent treatment with alkaline sulphite solution converted into brown *potassium o-tolueneazo- α -naphthalenediazosulphonate*, which on reduction with ammonium sulphide yielded brown, silky needles of the *potassium salt of o-tolueneazo- α -naphthylhydrazinesulphonic acid*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}\cdot\text{NH}\cdot\text{SO}_3\text{H}$. The violet-black, free acid, like its para-isomeride, reacted with aldehydes in the presence of alcoholic hydrogen chloride, with formation of arylidene derivatives of the corresponding *o*-tolueneazo- α -naphthylhydrazine; *o*-tolueneazo- α -naphthylsalicylidenehydrazine, deep brown crystals, m. p. 162° (*hydrochloride*, bluish-green powder); *cinnamylidene* compound, brown prisms with green lustre, m. p. 170° (*hydrochloride*, black, crystalline powder); *anisylidene* compound, brown leaflets, m. p. 153° (*hydrochloride*, dark blue leaflets); *p*-tolylidene compound, brown crystals, m. p. 152° (*hydrochloride*, black, crystalline powder).

m-Tolueneazo- α -naphthylamine, red crystals with blue lustre, m. p. 107° (*nitrate*, bluish-violet needles; *hydrochloride*, black, silky needles with $2\text{H}_2\text{O}$; *sulphate*, blue prisms), was prepared by the gradual addition of a solution of *m*-toluenediazonium chloride to an alcoholic solution of α -naphthylamine at 45° . In an analogous manner to its preceding *o*- and *p*-isomerides, this substance was successively converted into reddish-brown *potassium m-tolueneazo- α -naphthalenediazosulphonate* and *potassium m-tolueneazo- α -naphthylhydrazinesulphonate*, reddish-brown needles. The free *m*-tolueneazo- α -naphthylhydrazinesulphonic acid forms violet flocks and reacts with anisaldehyde and alcoholic hydrogen chloride, yielding *m*-tolueneazo- α -naphthylanisylidenehydrazine, a brown, crystalline powder, m. p. 159 — 160° ; *hydrochloride*, bluish-black, crystalline powder.

D. F. T.

Physical Changes in the Condition of Colloids. XXI. Protein Silver Salts. WOLFGANG PAULI and JOHANN MATULA (*Biochem. Zeitsch.*, 1917, **80**, 187—210).—The combination of proteins with silver salts was investigated by two methods, which gave parallel results, (a) by electrometric measurement of the changes in the Ag^+ concentration (in concentration cells), (b) by measurement of changes in electrical conductivity when proteins are added to silver salts. The changes were measured when different amounts of proteins were added to the same silver solution and when the same amount of protein solution was mixed with silver nitrate solutions of varying concentration. The proteins used were gelatin, serum-albumin (ox), and caseinogen. The results indicate a combination of the protein with silver nitrate. The amount of silver salt taken up from a given solution is not directly proportional to the amount of protein added, and the results obtained indicate a hydrolytic dissociation of the silver salt protein. The reaction appears to be a reversible one, like

that of the alkali salt-protein combination, and this statement receives confirmation from the fact that less silver salt is taken up by the protein in the presence of a salt of an alkali. Furthermore, the maximal amount of potassium chloride taken up by gelatin in a 1% solution is equal to about 2.2×10^{-4} gram equivalents of chlorine per gram of the protein, and about the same maximal amount of silver is taken up. Heated serum albumin combines with a larger amount of silver salt up to the concentration of 0.05*N*-solution, but the maximal amount found is the same as that of the unheated albumin solution. The silver salt-protein combination wanders to the anode in an electrical field in the same way as pure proteins. The conclusion is drawn that in the formation of combinations of proteins with silver salts and salts of alkalis and alkaline earths, the anionic and cationic parts are taken up in equivalent quantity by the proteins. In the formation of the insoluble protein-silver salt combination with albumin, several molecules of the silver salt are taken up by each molecule of protein before the insoluble precipitate is formed. S. B. S.

Specific Behaviour of Proteins. E. HEKMA (*Int. Zeitsch. phys.-chem. Biol.*, 1917, **3**, 122—132. Compare Diesselhorst and Freundlich, this vol., i, 180).—The author regards the specific behaviour of fibrin and other proteins as due to the property of existing in two forms, namely: (1) in an anisotropic, amorphous, and (2) in an anisotropic, liquid micellar-crystalline condition. When fibrin is placed in dilute alkali or acid, the swelling which occurs is caused by an adsorption of water into the molecules of fibrin, and the gradual passage of the fibrin gel into solution is regarded as the result of a change in the individual fibrin molecules from an isotropic solid to an anisotropic liquid-crystalline state. H. W. B.

Interesting Property of Old Solutions of Fibrinogen. P. NOLF (*Ann. Inst. Pasteur*, 1917, **31**, 155—160).—If a solution of fibrinogen is kept at 0° for some time, it gradually loses the property of clotting on the addition of fresh serum or a solution of thrombin. The clotting property is retained more readily by concentrated solutions of fibrinogen; dilute solutions, or those containing a trace of sodium carbonate, may lose the property within a few days, or at the latest within three or four weeks. The loss of clotting power occurs in stages; the clot formed after the first few days is found to be more flabby, tending to become viscous, and finally fails to become visible. This result is not due to the action of bacteria, since fibrinogen solutions can be kept at 0° for several months without betraying any sign of putrefaction.

The author explains the phenomenon by assuming that a gradual increase occurs in the stability of the fibrinogen molecules. Combination still ensues between thrombin and the stabilised fibrinogen, since a solution of the latter is found to possess distinct anti-clotting power, which is apparently to be ascribed to the capacity for withdrawing thrombin by adsorption without any formation

of fibrin. Moreover, by warming to 56° , which coagulates fibrinogen, the anti-clotting property disappears.

The hypothesis of the gradual transformation of one of the necessary factors in fibrin formation into an anti-clotting factor offers an explanation of the phenomena associated with the production of anti-clotting substances in the animal organism. The anti-substance present in peptone plasma, for instance, may be derived from fibrinogen. It is not stabilised fibrinogen, because its anti-clotting power is much greater and is not inhibited at 56° . The author, however, suggests that the liver may secrete a series of substances allied to fibrinogen possessing a common affinity for thrombin, but differing in solubility, molecular size, and temperature of coagulation. Substances opposing fibrinolysis would also be included in this series.

H. W. B.

Helicorubin. CH. DHÉRE and G. VEGEZZI (*Compt. rend.*, 1917, 164, 869—870).—In addition to the two bands already known in the absorption spectrum of alkaline helicorubin, the authors have discovered a third band at $\lambda=427\ \mu\mu$. Acidified helicorubin has a similar spectrum, except that the first band is twinned. When helicorubin, in acid solution, is shaken with air, it is oxidised, and the product has an absorption spectrum different from that of the original substance. It shows three bands: (1) from $\lambda 580$ to $\lambda 563$, (2) from $\lambda 547$ to $\lambda 519$, and (3) at $\lambda=415\ \mu\mu$. When helicorubin is acted on by acidified alcohol, it gives a helicohæmatin, which, when reduced in alkaline medium, gives a typical hæmochromogen. If helicorubin is oxidised by potassium permanganate and then reduced, the product shows an absorption band in the yellow at $\lambda=587\ \mu\mu$. With acetic or tartaric acids in the presence of sodium hyposulphite, helicohæmatin gives hæmatoporphyrin. Helicorubin is thus closely related to hæmoglobin, and acts without doubt in the intestine of the snail as a respiratory pigment.

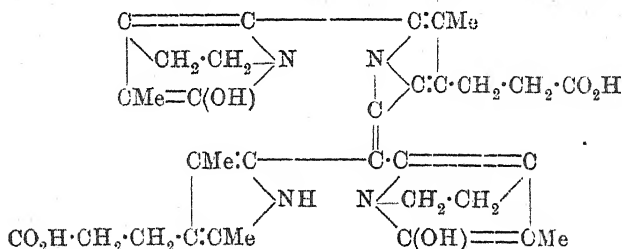
W. G.

Bile Pigments. X. Bilirubin-ammonia and Modifications of Bilirubin. WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1917, 99, 86—130. Compare A., 1915, i, 829).—The author describes a method for removing the compound containing sulphur which has been shown by Fischer (A., 1916, i, 515) constantly to occur in crystalline bilirubin as ordinarily prepared from the gallstones of the ox. Bilirubin-ammonia is first formed by the action of ammonia in dry methyl alcohol (*loc. cit.*). Two modifications of this substance are observed, the one, *A*, crystallising directly from the cold methyl alcohol solution, and the other, *B*, being precipitated from the mother liquor by ether. Bilirubin-ammonia-*A* is a stable substance and decomposes only slowly at 90° . The *B* modification is unstable and quickly undergoes oxidation at the ordinary temperature, forming a brown mass. On boiling with chloroform or extracting with chloroform vapour, both modifications yield bilirubins of slightly different properties which are designated bilirubin-*A* and -*B* respectively. At the same time, a

residue remains insoluble in chloroform, the amount of which is larger when the *B* form of bilirubin-ammonia is employed, but in both cases is found to be larger the longer the respective specimens of bilirubin-ammonia-*A* and -*B* have been kept. This insoluble substance contains the impurity shown by Fischer to be present in ordinary crystalline bilirubin; both bilirubin-*A* and -*B* are free from sulphur.

On analysis, bilirubin-*A* and bilirubin-*B* are both found to contain traces of chlorine derived from the chloroform used in their isolation. They are therefore again treated with ammonia and methyl alcohol, and the resulting ammonia compounds decomposed by boiling methyl alcohol. In this way two bilirubins, *A A* and *B B*, are prepared, giving figures on analysis which agree with the formula $C_{33}H_{36}O_6N_4$, originally proposed by Fischer, which is now definitely accepted by the author. The second of these bilirubins is even more easily oxidised and decomposed than bilirubin-*B*. Apparently the *A*-modification becomes partly converted into the *B* under the influence of ammonia, whilst the reverse change of *B* into *A* is favoured in the presence of chloroform. Between the orange *A* and the red *B* forms there are possibly several intermediate bilirubins.

From a consideration of the properties of and transformations undergone by bilirubin and its derivatives, the author is led to propose the following revised structural formula for the substance:



Corresponding formulæ are drawn for mesobilirubin, mesobilirubinogen, the xanthobilirubic acids, and other derivatives of bilirubin.

H. W. B.

Optical and other Properties of Pancreatin. M. A. RAKUZIN and (MLLE.) G. F. PEKARSKAJA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1314—1315).—Pancreatin, which exhibits both diastatic and peptonising properties, is usually regarded as a mixture of trypsin and diastase. This view is, however, not supported by the colour reactions of the three enzymes, and no decision is possible by means of the optical activity, since none of these enzymes is active. Pancreatin is adsorbed both by the electro-negative kaolin and, about twice as strongly, by the electro-positive aluminium hydroxide. Both adsorptions are irreversible, and both precipitate and filtrate exhibit the same colour reactions as the original pancreatin. At present it is, therefore, impossible to decide

if the adsorption is selective or non-selective, but further work in this direction is in progress. T. H. P.

The Inhibition of the Single Amyloclastic Functions of Amylase of Malt Produced by Keeping in the Presence of Various Reagents. T. CHRZĄSZCZ and A. JOSCHT (*Biochem. Zeitsch.*, 1917, 80, 211—241).—The action of malt amylase is regarded by the authors as being compounded of the action of two distinct ferments, one producing the liquefaction of starch, and the other its degradation to sugars. The production of dextrins (as determined by the iodine reaction) is either a resultant of the action of these two enzymes or is due to a special ferment. The method of experiment adopted was the determination of these various reactions with a sample of malt ferment which had been kept for various intervals in the presence of different reagents. The dextrinising action is inhibited in some cases more strongly, the more strongly is inhibited the liquefying action, whilst in other cases the inhibition runs more nearly parallel with the inhibition of the saccharifying power. For this reason, Wohlgemuth's iodine method for determining amyloclastic activity is open to objections, as amylase cannot be regarded as a single enzyme. For the preparation of amylase extracts, glycerol in appropriate concentration in water, and aqueous solutions of pyridine and quinoline are most suitable, as they cause the smallest amount of inhibition of the various amyloclastic functions when the ferment preparation is kept for a long time in their presence. Pure water, solutions of alcohols, acetone, and chloroform are not suitable. Bases in suitable concentrations have a favourable action on the liquefying and dextrinising functions, but inhibit the saccharifying function. Alcohols inhibit all functions, but more especially the liquefying and dextrinising. S. B. S.

Mechanism of Oxydase Action. G. B. REED (*Bot. Gaz.*, 1916, 62, 53—64).—There exists a considerable body of data which indicates that all oxydases are made up of two constituents: a peroxide-like substance or oxygenase and a substance capable of activating this peroxide or a peroxydase. Further light has been thrown on the reaction by investigating the effect of platinum-black as a catalyst. A large platinum crucible was coated with a deposit of the colloidal metal and exposed to nascent oxygen by making it the anode in a dilute solution of hydrochloric acid through which an electric current was passed. The crucible was then immersed in the solution to be oxidised. Oxidation took place in proportion to the amount of oxygen furnished by the charged platinum and additive effects were obtained by removing and recharging the crucible. As a basis of comparison, the rate of oxidation was next determined, when hydrogen peroxide was used as an oxidising agent and platinum-black as a catalyst. In comparing the curves for the rate of oxidation obtained by the two methods, it became evident that by starting with a sufficient charge of oxygen on the platinum-black and by renewing it often enough,

the curves could be made exactly similar. It appeared likely, therefore, that the hydrogen peroxide acted by continually recharging the platinum-black with oxygen, and this hypothesis was fully confirmed by following out the variations in oxidation potential which occurred in the different phases of the reaction.

L. M. U.

Mode of Action of Plant Peroxydases. G. B. REED (*Bot. Gaz.*, 1916, 62, 233—238).—Following on the lines of the previous experiments, the platinum-black was replaced by a plant peroxydase. About 150 grams of finely chopped horseradish root were extracted with 300 c.c. of water. The solution behaved like the platinum-black: alone it produced no oxidation, but as soon as it was charged with oxygen by treatment with potassium permanganate, oxidation occurred in the measure of the charge, and additive effects were obtained by treating the peroxydase solution a second time with potassium permanganate. Potato peroxydase gave exactly similar results, and the author concludes that in oxidation processes catalysed by peroxydases, two reactions are involved: the peroxydase combines with oxygen from the oxygenase to form an intermediate compound which is a more energetic oxidising agent than the original source of the oxygen.

L. M. U.

The Relation between Oxydase and Catalase in Plant Tissues. G. B. REED (*Bot. Gaz.*, 1916, 62, 409—412).—Although peroxydases usually decompose hydrogen peroxide, the experiments with platinum-black (see preceding abstracts) would indicate that the action of the peroxydase is independent of its ability to decompose hydrogen peroxide. In order to throw more light on the question, pineapple juice was pressed out of fruits at different stages of ripeness, and was examined for catalase and peroxydase activity. Catalase activity was measured by the direct decomposition of hydrogen peroxide, whilst peroxydase activity was measured by the oxidation of pyrogallol by hydrogen peroxide. Different fruits exhibited great variation in their catalase activity, but scarcely any in their peroxydase activity. The author therefore concludes that the substances which effect the decomposition of hydrogen peroxide are not of necessity concerned with the enzymes which accelerate peroxide oxidations.

L. M. U.

Significance of Colour Changes in Oxydase Reagents. Separation of Oxydase Reactions from the Catalase Reaction. G. B. REED (*Bot. Gaz.*, 1916, 61, 430—432; 62, 303—308; from *Physiol. Abstr.*, 1917, 2, 197, 198).—The author has compared the efficiency of the different colour reagents used for work on oxydases with regard to the amount of oxidation required to give an appreciable colour change. The volume of standard permanganate required to give the minimum colour change to 0.1*M*-solution of reagent varied from 0.5 c.c. with dimethyl-*p*-phenylenediamine to 10.0 c.c. with quinol.

In the second paper the author opposes the view that the cata-

lase action, in which hydrogen peroxide is decomposed with liberation of molecular oxygen, is in any way causally associated with peroxydase decomposition of hydrogen peroxide in oxidation reactions. He finds that the two types of activity with colloidal platinum do not show any correlation. A colloidal platinum surface charged with hydrogen continues to decompose hydrogen peroxide much faster than if charged with oxygen, but as regards peroxydase activity, while oxidising formaldehyde in the presence of the peroxide, the platinum in its two states is identical. Measurement of the oxygen potentials of the two states shows that, whilst widely divergent in the first minute, they both shift to the same mean oxygen potential in a few minutes. G. B.

Periodic Phenomena shown by Ferments. J. TEMMINCK GROLL (*Arch. Néerland. Physiol.*, 1917, 1, 403—424. Compare Arrhenius, *Immunochemie*, 1907).—The activity of urease at 35° when plotted against time gives a sinusoidal curve, the activity becoming alternately weaker and stronger. At 65° a unimolecular curve is obtained, as given by Arrhenius (*loc. cit.*). At intermediate temperatures (45—55°) the curve is a combination of the two. It is suggested that this is a consequence of the colloidal nature of the ferment; and in support of this view the catalytic decomposition of hydrogen peroxide by colloidal platinum and gold has been further examined. Definite results could not, however, be obtained, as the oscillation of the activity of these catalysts is so rapid that the phenomenon is not clear. W. G.

Physiological Chemistry.

The True Nature of the "Acidotic Condition" of Infants. K. A. HASSELBALCH (*Biochem. Zeitsch.*, 1917, 80, 251—258).—In attempting to ascertain the true reaction of the blood in the diagnosis of acidotic conditions, care should be taken to make the estimation in the presence of a sufficient tension of carbon dioxide. If this is not done, the concentration of the oxy-hæmoglobin will be the most important factor in the result, as it is a fairly strong acid. From the point of view of these facts, the author criticises some conclusions drawn by Ylppö on the supposed acidosis in new-born infants, in which the precaution above mentioned was neglected; the author contends, therefore, that this acidosis of the new-born infant does not exist. S. B. S.

The Ammonia Content of the Blood. II. V. HENRIQUES and E. CHRISTIANSEN (*Biochem. Zeitsch.*, 1917, 80, 297—311).—When ammonia is estimated in the blood by Folin's aeration

method, care must be taken not to allow the temperature to rise too high. If the temperature is maintained below 20° , the same amount of ammonia is obtained, whatever base is used to make the blood alkaline (sodium carbonate, lime water, or magnesium oxide). At higher temperatures (45°), however, larger amounts of ammonia are obtained when sodium carbonate is used. All bases give rise to more ammonia from the blood at 45° than at 16° . The ammonia is obtained in larger quantities from the corpuscles than from the plasma. The quantity of ammonia in the case of carnivorous animals is larger in the blood of the portal vein than in the blood of the arteries, even when the animals have fasted for eight days. This marked difference is not observed in the case of dogs. Arterial and venous bloods contain the same amount of ammonia.

S. B. S.

Experimental Glycosuria. XII. Production of Lactic Acid in the Blood following the Injection of Alkaline Solutions of Dextrose or of Alkaline Solutions alone. J. J. R. MACLEOD and D. H. HOOVER (*Amer. J. Physiol.*, 1917, **42**, 460—465; from *Physiol. Abstr.*, 1917, **2**, 119. Compare this vol., i, 367).—The control of the blood sugar level is effected, not by changes in the glycogenic function in liver and muscles, or by oxidation of the dextrose in the muscles, but by destruction of the sugar in the blood itself. Samples of blood collected in different parts of the circulation show that lactic acid increases there when alkaline solutions, but not when acid solutions, of dextrose are injected. Some enzyme in the blood, of the glyoxalase class, is considered to be responsible for the change.

G. B.

The Residual Reduction of the Blood Considered in Relationship to the Reducing Components of the Residual Nitrogen. JOH. FRIGL (*Biochem. Zeitsch.*, 1917, **80**, 330—332).—Chiefly a discussion of the part played by creatine and creatinine in contributing to the "residual reduction" (of alkaline copper solutions, etc.) by the blood.

S. B. S.

Prothrombin and Thrombin (Free and Combined) in Blood Serum. H. S. GASSER (*Amer. J. Physiol.*, 1917, **42**, 378—394; from *Physiol. Abstr.*, 1917, **2**, 115).—There is only one kind of thrombin; it may be formed from prothrombin (by calcium and thromboplastin) or liberated from combination with anti-thrombin by alkali activation. This inactive compound is believed to exist because (1) the inactivation of thrombin by non-specific colloids, such as charcoal, is negligible compared with that produced by plasma; (2) if serum is kept, both antithrombin and combined thrombin disappear at the same time; (3) combined thrombin is destroyed by heat at the critical temperature of anti-thrombin (not at that of thrombin); (4) in alkali activation, thrombin is destroyed; (5) when thrombin is incubated with anti-thrombin (that is, plasma heated at 60°), a combination is formed which does not clot fibrinogen until activated by alkali. Thrombo-

plastin does not liberate combined thrombin. The amount of prothrombin in serum varies inversely as the amount of tissue extract present at the time of clotting. The amount of thrombin formed in the presence of a given amount of thromboplastic substance is definite in amount; it forms rapidly and is combined rapidly, the system then returning to equilibrium. This rapid inactivation by the plasma, which is intolerant of free thrombin, maintains the fluidity of the blood.

G. B.

Applicability of Schulze's Law to Complement. E. POYARKOV (*C. R. Soc. de Biol.*, 1917, **80**, 239—241).—The action of complement is known to be slowed or inhibited by solutions of the salts of the alkaline earths. The author has investigated the complement of the spermyolysin of normal rabbit's serum, and finds that the effect of neutral salts depends greatly on the valency of the cation. He has determined the concentrations of various salts which render the action of the complement most rapid; a concentration of 43—60 millimolecules of various sodium salts corresponds with 5—7 millimolecules for barium, strontium, and calcium chlorides, and with 0.2 millimolecule for aluminium chloride, and hence there is a close correspondence with the precipitation of lyophobic sols (for example, of arsenious sulphide). The author deduces from this applicability of Schulze's law that the complement is a negative suspension colloid, and therefore not a protein, but a lipid. Among lipoids, lecithin does not obey Schulze's law, but cholesterol does. In general, the results support the colloidal theory of immunity (Bordet) rather than the physicochemical theory (Ehrlich, Arrhenius).

G. B.

Production of Light by Animals. E. TROJAN (*Int. Zeitsch. phys.-chem. Biol.*, 1917, **3**, 94—105).—A discussion of the reasons why certain animals should emit light and of the possible ways in which the light is produced.

H. W. B.

Bio-luminescence and Metabolism. ROBERT HELLER (*Int. Zeitsch. phys.-chem. Biol.*, 1917, **3**, 106—121).—The author advances the theory that the phenomenon of bio-luminescence is associated with the last phases in the catabolism of those nitrogenous substances which are eliminated as purines from the animal organism. According to his unpublished results, hypoxanthine, guanine, xanthine, theobromine, and other purines exhibit an intense photophosphorescence.

H. W. B.

Selective Adsorption of Antidiphtheritic Serum by Aluminium Hydroxide. M. A. RAKUZIN and G. D. FLIER (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1324—1330).—It has been shown previously that the adsorption of enzymes and toxins, especially by aluminium hydroxide, is in most cases selective, and the investigations have now been extended to antidiphtheritic serum.

The serum employed, D¹⁵ 1.0340, $[\alpha]_D -28.876^\circ$, was straw-yellow and of neutral reaction. It gave the following protein

colour reactions, with the degrees of sensitiveness indicated in brackets: biuret (1:660), Millon's (1:330), Liebermann's (1:2500); Adamkiewicz's (1:9000), xanthoprotein (1:660), Molisch's (1:330), Pettenkofer's (1:1250), and Ostromisslenski's (1:1250). The adsorption by aluminium hydroxide proceeds irreversibly and with quantitative separation of the toxin, the proportion of the latter adsorbed being 43.47%. The liquid remaining after the adsorption is colourless and neutral, and gives all the above colour reactions of the proteins. T. H. P.

The Nature of Mountain Sickness. ERWIN RIPPSTEIN (*Biochem. Zeitsch.*, 1917, 80, 163—186).—If rats are exposed in a chamber to diminished pressure, they exhibit symptoms analogous to those of mountain sickness. These appear when the air pressure is diminished to about 209 mm. of mercury (161.4 mm. reduced pressure), corresponding with the partial oxygen pressure of 27.68. If the chamber is filled with pure oxygen and the pressure is then diminished, the symptoms appear at the pressure of 91.25 mm. (41.25 mm. reduced), corresponding with the partial oxygen pressure of 23.48 mm. In experiments in which the air of the chamber was partly replaced by nitrogen and the pressure then diminished, the symptoms appeared at the pressure 459.90 mm., at which the partial oxygen pressure was 29.10. Carbon monoxide poisoning of moderate grade causes similar symptoms at ordinary barometric pressure. The conclusion is drawn that diminution of oxygen is the essential cause of mountain sickness, as the symptoms in all the experiments set in when the partial oxygen pressure was about the same, and the mechanical action on the lungs only appears when the barometric pressure is exceptionally low. S. B. S.

Selective Adsorption of Denys's Tuberculin by Aluminium Hydroxide. M. A. RAKUZIN and G. D. FLIER (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1316—1319).—Two samples of tuberculin, prepared by (1) Vermel, Moscow, and (2) the Institut de Bactériologie de Louvain, have been examined. Both preparations are straw-yellow and neutral, and the other physical properties are: (1) D^{15}_D 1.0223, $c=6.3134$, $[\alpha]_D -9.81^\circ$, and (2) D^{15}_D 1.01944, $c=2.285$, $[\alpha]_D -21.22^\circ$. Both contain free ammonia and show Adamkiewicz's, Molisch's, Pettenkofer's, Ostromisslenski's, Liebermann's, and the xanthoprotein reactions, but the limits of sensitiveness differ widely in the two cases; only the Louvain preparation gives Millon's reaction, and neither gives the biuret reaction. Aluminium hydroxide adsorbs 7.62% and 23.08% of the respective preparations, and both adsorptions are irreversible as regards boiling water. With reference to the colour reactions of the proteins and to the rotatory power, the products of adsorption behave similarly to the original tuberculins. T. H. P.

The Resorption and Change of Abnormally Large Amounts of Sucrose and Invert-sugar. C. BRAHM (*Biochem. Zeitsch.*, 1917, 80, 242—250).—Sugar was found neither in the

urine nor fæces after ingestion of as much as 300 grams of sucrose and invert-sugar (artificial honey) by man and dog. In one case as much as 600 grams were ingested in one day by a man, and even after this amount no sugar could be detected in the excreta.

S. B. S.

Intravital Staining with Acid Dyes and its Significance for Anatomy, Physiology, Pathology, and Pharmacology.

WERNER SCHULEMANN (*Biochem. Zeitsch.*, 1917, 30, 1—142).—Two main problems have been considered by the author: (1) the rate of dissemination and elimination of the dyes after injection; (2) the storage of the dyes in the cells. Experiments have been carried out as far as possible with dyes of known and similar constitution, chiefly belonging to the trypan-blue and benzopurpurine groups and carbamide derivatives. There appears to be no relationship between chemical constitution and capacity for intravital staining, and the side-chain theory of Ehrlich will not explain the action of the dyes when injected into the living organism. On the other hand, experiments carried out for the author by Wilborn show that there is an intimate relationship between the rate of diffusion of dyes in gelatin gels and their capacity for intravital staining. Dyes which diffuse slowly are taken up chiefly by cells near the point of injection, whereas those which diffuse rapidly become quickly disseminated through the organism and eliminated. Other dyes have an intermediate character, and are disseminated with sufficient rapidity without being eliminated too quickly by the organism, and these are well adapted for intravital staining. The methods of taking up dyes and their storage by the cells are also discussed in great detail by the author, who directs attention to the relationship between amœboid movement, phagocytic action, and capacity for being stained by acid dyes, and the influence of surface tensions at interfaces and other physical characters on these factors. The nature of the "granula" and of "metachromatism" (the differences of colour of the dyes in different cells) is also discussed. Evidence is brought forward to show that "metachromatism" is due to the difference of the state of aggregation of the dyes under different conditions, such as the variation in the amount and character of the electrolytes. S. B. S.

Theoretical Considerations Relative to the Intravital Staining with Acid Dyes.

WERNER SCHULEMANN (*Kolloid Zeitsch.*, 1917, 20, 113—118).—The author discusses the distribution of acid dyes in living organisms on the basis of experiments which are to be published elsewhere. The distribution is to a very large extent dependent on the physical condition of the dye in solution. The size of the particles not only affects the ultimate distribution, but also the rate at which the organism is coloured by the dye. The general coloration of an organism is apparently only attainable by the use of dyes which are molecularly disperse.

H. M. D.

The Physico-chemical Properties of the Products of the Group of the Arsenobenzenes. Their Transformation in the Organism. J. DANYSZ (*Ann. Inst. Pasteur*, 1917, 31, 114—137).—From a study of the four compounds, diaminodihydroxyarsenobenzene, luargol, galyl (diphosphaminotetrahydroxyarsenobenzene), and novoarsenobenzene, it would appear that the first three have the characteristic properties of colloids, luargol being the most colloidal and galyl the least. Novoarsenobenzene possesses more the properties of a salt. The first three compounds when intravenously injected are converted into insoluble compounds, the precipitates thus formed being then redissolved by certain organic bases, giving stable, soluble compounds which are eliminated in the urine, this dissolution being probably largely controlled by the leucocytes. The last part of the paper is a summary of the present state of knowledge with reference to the toxicity of and intolerance for these compounds. W. G.

Chemistry of Vegetable Physiology and Agriculture.

The Formation of Ferments. II. MARTIN JACOBY (*Biochem. Zeitsch.*, 1917, 80, 357—363. Compare this vol., i, 305).—In continuation of the investigations on bacteria containing urease, it is shown by the author that these flourish and produce the enzyme when they are grown on Uschinski's medium when this contains traces of bouillon which is added to the medium in making the sub-culture of the bacteria originally grown on bouillon. In the absence of traces of this material, the bacteria remain alive and capable of reproduction, but their growth is considerably inhibited. Uschinski's medium contains glycerol, sodium and calcium chlorides, magnesium sulphate, dipotassium phosphate, ammonium lactate, and sodium aspartate. S. B. S.

The Effect of Some Acids and Alkalis on Soil Bacteria in the Soil Solution. OSWALD M. GRUZZI (*Soil Sci.*, 1917, 3, 289—295).—A solution was extracted from a rich sandy soil by the paraffin oil method; from it were prepared three experimental solutions, one of which was made neutral, another alkaline (*N*/446·4), and the third acid (*N*/1200), using sodium hydroxide and hydrochloric acid for the purpose. Ten c.c. of each solution were then inoculated into sterile sand and incubated, bacterial counts being made at intervals for two hundred and twenty days. In the alkaline medium the bacterial numbers remained nearly constant for eighteen days, then rose to about 150% of the original numbers; by the sixtieth day, when the medium gave an acid reaction, the numbers had fallen again to below the original level and continued to fall for another seventy days. In the neutral

medium, which had become acid on the eighteenth day, the numbers of bacteria decreased gradually from the very start until the fifth month. Finally, in the acid medium, the numbers fell rapidly to almost nothing and remained at a very low level for the whole two hundred and twenty days.

The experiment was repeated, using a solution from a sandy loam and sulphuric acid in the place of hydrochloric acid. The solutions in this case were made up to *N*/1200, *N*/1400, *N*/2164, and *N*/2840 acid and *N*/412, *N*/990, and *N*/1040 alkaline. Bacterial numbers in the alkaline media multiplied rapidly to between five and six times the original numbers, and then fell as before, the maximum point of development occurring a few days later with the two stronger than with the weaker solution. The *N*/2164 acid medium remained with approximately the same number of bacteria throughout the experiment, and stronger solutions caused immediate depression of bacterial numbers, but with the *N*/2840-acid the bacteria first increased to about three times their original numbers and then decreased.

L. M. U.

Soil Bacteria and Phosphates. C. G. HOPKINS (*Science*, 1916, [*N.S.*], 44, 246—249; from *Physiol. Abstr.*, 1917, 2, 149).—Nitrite bacteria render soluble the phosphorus and calcium of insoluble phosphates in the process of converting ammonia into nitrite, corresponding with the equation $4\text{HNO}_2 + \text{Ca}_3\text{P}_2\text{O}_8 = \text{CaH}_4\text{P}_2\text{O}_8 + 2\text{CaN}_2\text{O}_4$. Neither ammonia-producing nor nitrate-producing bacteria have any appreciable effect in liberating soluble phosphorus. For full details see *Univ. Illinois Agric. Exper. Station Bull.* No. 190.

G. B.

The Reducing Ferments. A. BACH (*Arch. Sci. phys. nat.*, 1917, [iv], 43, 307—316).—The first part of the paper is a more detailed account of work already published (compare this vol., i, 375). The author notes the injurious effects of the aldehydes and of the products of reduction of the nitrates, notably hydroxylamine, on the catalytic power of the reducing ferment of milk. There are other factors which have not yet been elucidated.

W. G.

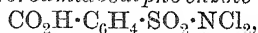
Nitrification in Semi-barren Soils. W. P. KELLEY (*J. Agric. Research*, 1916, 7, 417—437; from *Chem. Zentr.*, 1917, i, 679—680).—An account is given of laboratory and field experiments which have extended over a number of years. The experiments were performed partly according to a modification of Remy's solution process, but mainly with the soil itself, the latter serving as culture medium. Dried blood (13·20% N) in quantities varying from 0·0625 to 1%, bone meal (4·25% N) from 0·25 to 4%, and ammonium sulphate (21% N) from 0·0375 to 0·6%, were used as sources of nitrogen. Nitrates were generally estimated by the phenoldisulphonic acid process, sometimes also by reduction with aluminium; the methods yield concordant results. Experiments showed that the amounts of nitrate which are formed during four

weeks from blood, bone meal, and ammonium sulphate varied greatly with the differing concentrations, both with respect to the absolute amount and also to the proportion of nitrogen converted. Feeble or, in certain soils, negative nitrifying power was observed with 1% of blood, whilst, in the same circumstances, strong action was found with 1% of bone meal or 0.2—0.3% of ammonium sulphate. When, on the other hand, smaller concentrations of blood were used, such as are customary in field experiments, powerful nitrification was invariably caused. When equal amounts of nitrogen were employed, similar amounts of nitrate were formed whether from blood, bone meal, or ammonium sulphate. High concentrations of bone meal, with a nitrogen content corresponding with that of 1% of blood, have a more poisonous effect on nitrification than the latter. Experiments with widely differing varieties of soil from South California showed that the inability to nitrify 1% of blood is not limited to any particular variety of soil or to soils which have a low content of organic substances.

The addition of alkali salts caused divergent action according to the concentration of the source of nitrogen. In one soil, 0.05% of sodium carbonate was distinctly poisonous to the nitrification of 1% of blood, whereas 0.4% had no action towards 0.1% of blood. Similarly, 0.1% sodium carbonate was poisonous towards 0.15% ammonium sulphate, but distinctly stimulating to 0.0625%. It is further shown that very contradictory conclusions can be drawn from laboratory experiments when the period of action is altered. Nitrites were found in large quantity when excessive amounts of nitrogenous material were used; in certain cases the quantity of nitrite exceeded that of nitrate when the experiments were prolonged for several weeks. Addition of alkali salts can depress the formation of nitrates, whilst, at the same time, nitrites are produced. In the estimation of nitrate it is necessary to take the presence of nitrite into account, the error involved being much greater with the aluminium reduction method than with the other process. According to the author, it appears very probable that the results of previous investigations on nitrification are less valuable than those derived from experiments in which the conditions are made to approximate as closely as possible to those of field trials. (Compare Löhnis and Green, *Chem. Zentr.*, 1915, i, 497; Allen and Bonazzi, *Ohio Agr. Exp. Stat. Bull.*, 1915, 7.) H. W.

The Apiculate Yeasts. E. KAYSER (*Compt. rend.*, 1917, 164, 739—741).—The apiculate yeasts are very resistant to acids, giving an active fermentation even in the presence of 2.5% of citric acid or 0.2% of sulphuric acid, but under such conditions they gradually lose, in successive generations, their characteristic form and become oval or round. The presence of acids thus favours their development in a must of beetroots and apples, and exerts a marked influence on the products of fermentation, giving more volatile products and less alcohol. Rise in temperature also causes the production of larger amounts of volatile esters. W. G.

Disinfection of Drinking-water: with a Description of a New Substance for the Preparation of Stable Tablets for the Sterilisation of Polluted Water. H. D. DAKIN and E. K. DUNHAM (*Brit. Med. Journ.*, 1917, i, 682—684).—Sodium *p*-toluenesulphochloroamide (chloroamine-T) (A., 1916, i, 533) only acts in acid solution at low concentrations, and tablets of this substance, mixed, for instance, with citric acid, are unstable on keeping. For this reason a carbonyl group has been incorporated in the molecule. *p*-Dichloroamidodisulphobenzoic acid,



is prepared by oxidising *p*-toluenesulphonamide with sodium dichromate to *p*-amidodisulphobenzoic acid and then chlorinating. The new substance, stout prisms from acetic acid, m. p. 213°, sterilises water in thirty minutes at a concentration of 1:300,000, and a solution of this strength is almost tasteless. It may be conveniently used as tablets containing 4% of the substance, 4% of sodium carbonate, and 92% of sodium chloride. One tablet, weighing 0.1 gram, would then sterilise 1 litre of water. G. B.

A Simple and Rapid Method of Studying Respiration by the Detection of Exceedingly Minute Quantities of Carbon Dioxide. A. R. HAAS (*Science*, 1916, [N. S.], 44, 105—108).—In order to determine the effect of solutions on respiration, a new method has been devised for detecting minute quantities of carbon dioxide in solution. A piece of plant tissue is placed in a measured amount of the test solution with a given quantity of phenolsulphonephthalein as indicator, and the amount of carbon dioxide given off is measured by the colour developed. The method is extremely sensitive, rapid, and simple, and the amount of carbon dioxide given off in successive intervals can be estimated without disturbing the tissue. L. M. U.

Carbohydrate Metabolism in the Green Leaf. W. GAST (*Zeitsch. physiol. Chem.*, 1917, 99, 1—53).—The author has estimated the dextrose, lævulose, maltose, and sucrose in the leaves of *Tropaeolum majus*, *Cucurbita ficifolia*, *Vitis vinifera*, *Musa Ensete*, and *Canna iridiflora* gathered at noon and shortly before daybreak, when the metabolic activities of the plants are at their highest and lowest points respectively.

In all cases, the sugar present in largest amount is sucrose. It reaches a maximum during the day and diminishes during the night. In *Canna*, sucrose constitutes 90% of the total sugars by night as well as by day. In the other cases, the percentage of sucrose is usually about 50 in the leaves taken at noon and between 40 and 45 in those gathered at night. Maltose, dextrose, and lævulose occur in varying proportions in different plants, and do not show any constant rise or fall during the twenty-four hours.

These results confirm those of previous workers, and are in accord with the view that the first recognisable product of assimilation in the green leaf is sucrose. H. W. B.

Nitrate and Nitrite Assimilation. XII. OSKAR BAUDISCH (*Ber.*, 1917, **50**, 652—660. Compare A., 1916, i, 699—702).—The author has already directed attention to the importance of organic complexes containing iron or magnesium in the processes of oxidation and reduction which go on in the living organism. He has now discovered that when a solution of a hexose or lactose is warmed with a small quantity of an iron salt and sodium carbonate, a dark brownish-reddish-violet solution may be obtained in which the iron does not react with hæmatoxylin, but which has specific reducing properties. For example, it reduces nitrobenzene to aniline, which the alkaline sugar solution alone will not do. Furthermore, it reduces nitrites, but not nitrates. The reduction is catalytic, for a small quantity of the iron solution reduces relatively large quantities of a nitrite, the products being ammonia and substances of the nature of aldehydic amines. The hypothetical acid, NOH, is again to be regarded as representing a critical, intermediate stage. J. C. W.

A Dynamical Theory of Antagonism. W. J. V. OSTERHOUT (*Proc. Amer. Phil. Soc.*, 1916, **55**, 533—553).—The electrical resistance of *Laminaria Agardhii* was determined in 0.52*M*-sodium chloride, in 0.278*M*-calcium chloride, and in various mixtures of these salts. In pure sodium chloride, the resistance fell from the first, but with all the other solutions, the resistance first rose and then fell. To account for this phenomenon, the author assumed: (1) that two processes were involved, and that the resistance was determined by a substance *M*, which was formed and broken down according to the reaction $A \rightarrow M \rightarrow B$; (2) that calcium chloride accelerated the reaction $A \rightarrow M$; and (3) that both sodium chloride and calcium chloride combined with a substance in the protoplasm to form a compound which inhibited the reactions $A \rightarrow M$ and $M \rightarrow B$. Then, by ascribing suitable values to all the factors involved, theoretical curves of resistance were obtained which approximated closely to those plotted from the experimental results. The author points out that whether the assumptions do or do not represent actual facts, it is clear that there are two processes involved, one of which produces a rise and the other a fall of resistance, and that their speed may be regulated by varying the proportions of sodium chloride and calcium chloride. Further, the theory enables the resistance of cells to be predicted in any mixture of the salts and at any given time during exposure. L. M. U.

Antagonism and Weber's Law. W. J. V. OSTERHOUT (*Science*, 1916, [N.S.], **44**, 318—320).—The dynamical theory of antagonism (outlined above) is used to explain Weber's law of the direct proportionality of antagonistic substances. By the union of the two antagonistic salts with the protoplasm, a substance is formed which inhibits death or injury. Assuming that this compound is formed in a surface, the amount formed will be independent of variations in concentration in the solution, and

will depend only on the proportion which the antagonistic salts bear to one another. L. M. U.

The Penetration of Balanced Solutions and the Theory of Antagonism. W. J. V. OSTERHOUT (*Science*, 1916, [*N. S.*], **44**, 395—396).—Antagonism has been explained by assuming that antagonistic substances prevent each other from entering the cell, but this explanation is not satisfactory, as it has been shown that penetration does occur when a cell is in a balanced solution, although at a slower rate than when in an unbalanced solution. As a way out of the difficulty, the author suggests that the antagonistic substances affect certain life processes which consist of consecutive reactions of the type $A \rightarrow M \rightarrow B$ (see this vol., i, 434), where M is a substance which determines, not only the electrical resistance of the protoplasm, but also its permeability to salts. Provided, therefore, that the substances are present in proportions which do not inhibit the life process, a certain amount of penetration may be expected to occur. L. M. U.

Permeability. IV. The Action of Various Organic Substances on the Permeability of the Plant Cell, and its Bearing on Czapek's Theory of the Plasma Membrane. WALTER STILES and INGVAR JØRGENSEN (*Ann. Bot.*, 1917, **31**, 47—76).—Disks of potato tissue were immersed in solutions of various organic substances (alcohols, acetone, chloroform, ether, chloral hydrate, urethane, aniline, pyridine), and the effect of these substances on the permeability of the plasma membrane was determined by measuring the rate of exosmosis; the rate of exosmosis in its turn was measured by the electrical conductivity of the solution. It was found that in all cases the rate of exosmosis increased with the concentration of the solution employed, but equimolecular solutions of the different substances did not bring about the same degree of exosmosis; in the homologous series of the monohydric alcohols, the more complex the molecule the greater the exosmosis produced. No evidence was obtained of the existence for any solution of a critical concentration below which the exosmosis of electrolytes would not take place. The authors show that the rate of exosmosis produced by a solution cannot be a function of its surface tension alone, also that other assumptions used by Czapek in formulating his theory of the plasma membrane are untenable. From the ordinary laws of mass action, they deduce a mathematical expression connecting time and exosmosis, and the curve representing this equation is of the same form as those obtained from the actual experimental figures. L. M. U.

Permeability and Viscosity. W. J. V. OSTERHOUT (*Science*, 1916, [*N. S.*], **43**, 857—859).—It has been suggested recently that the permeability of the surface layer of protoplasm is determined by its viscosity, which in turn depends on its colloidal condition. Increased permeability may be produced by decreased viscosity and vice versa, but in the second case if the increased viscosity

goes beyond a certain point, a change occurs in the degree of intimacy between disperse phases and solvent with a sudden increase in permeability. The author applies this hypothesis to the results he obtained when determining the permeability and the electrical resistance of *Laminaria*, but finds that in several instances the theoretical deductions do not agree with the facts actually observed.

L. M. U.

The Physiological Significance of Calcium in Plants.

T. ROBERT (*Rev. gén. Sci.*, 1917, **28**, 101—108; from *Physiol. Abstr.*, 1917, **2**, 192—193).—Largely a review of the theories in regard to the action of calcium in plants. Experiments of the author on *Penicillium glaucum* and *Aspergillus niger* led him to the conclusion that small quantities of calcium sulphate (up to 0.01%) do not accelerate growth; somewhat larger quantities (0.04%) produce a slight increase in weight, due to fixation of the metal as oxalate. Above 0.4% calcium is toxic. Contrary to Osterhout's opinion, calcium has no antagonistic action in cultures of fungi.

G. B.

The Micellary Theory of Nägeli as a Working Hypothesis in the Investigation of Chemical and Physical Changes in Cotton Fibres, with Special Reference to the Processes of Dyeing.

R. HALLER (*Kolloid Zeitsch.*, 1917, **20**, 127—145).—The chemical and physical properties of cotton fibres lead to the conclusion that the outer membrane consists of two structural elements which show but small differences under normal conditions. When the cellulose is transformed into hydrocellulose and oxycellulose, the two components are much more readily differentiated. The difference is shown in the behaviour towards chemical reagents and in the appearance under the ultra-microscope. The proof that two such structural elements are involved is said to afford evidence in support of Nägeli's micellary theory of the structure of vegetable membranes. The absorption of mordants and dyes by the penetration of these substances into the micellary interstices is dependent on the degree of dispersity of the particles. The power of penetration is limited to particles of diameter less than about 5 $\mu\mu$. In the case of mercerised fibres, the micellae are more widely separated than in the original untreated fibres, and particles of larger size than those above referred to may accordingly be absorbed, with the result that the depth of colour is greater.

H. M. D.

Pectin Substances. I. SVEN ODÉN (*Int. Zeitsch. phys.-chem. Biol.*, 1917, **3**, 71—82).—The author demonstrates the presence of insoluble, or almost insoluble, acid substances in various plant tissues by a method based on the change in the electrical conductivity of an aqueous suspension of the tissue which occurs on the addition of a small amount of ammonium hydroxide. The plant

tissue after washing is brought to a finely divided state by prolonged grinding with water, and is then freed from traces of electrolytes by repeated centrifugalisation with pure water. Equal amounts of ammonia are added to equal volumes of the aqueous suspension and of pure water respectively; and a greater increase in the electrical conductivity in the former than in the latter case indicates the presence in the plant tissue of acid pectin substances, which form readily dissociated ammonium salts. The addition of dilute hydrochloric acid to the filtered ammoniacal suspension yields a gelatinous precipitate of the insoluble acid pectin substance (compare Schryver and Haynes, this vol., i, 245).

The author claims that these pectin substances, besides acting as the binding material of plant tissues, constitute a means for regulating the content of hydrogen and hydroxyl ions in the circulating fluids in the tissues and maintaining the cell-contents in a slightly acid condition. They form a reserve of insoluble acid, which is nevertheless readily available for the neutralisation of any alkaline substance brought into contact with the cell. H. W. B.

The Form of Iodine in Marine Algæ. Y. OKUDA and T. Eto (*J. Coll. Agric. Imp. Univ., Tokyo*, 1916, 5, 341—353; from *Physiol. Abstr.*, 1917, 2, 195).—Various fresh algæ (*Ecklonia*, *Turbinaria*, *Sargassum*) were found to contain only a minute quantity of iodides. Nearly all the iodine is in organic combination. The greater part of the iodine is in a form soluble in water, strong alcohol, dilute alkalis, or acids. It is not a protein compound. Concentrated solutions of sulphuric acid and sodium hydroxide decompose it completely. Decomposition is also brought about by micro-organisms, but there is no enzyme in the plant to effect this.

Old algæ contain more iodine than young plants, and those growing in the open sea more than plants of the same species in inland waters. The greater part of the iodine easily diffuses from dead algæ into fresh- or salt-water, so that drifted algæ are unsuitable for the preparation of iodine. G. B.

Chemical Investigation of the Substance of the Birch. GEORG GRASSER (*Collegium*, 1916, 445—452; from *Chem. Zentr.*, 1917, i, 413. Compare A., 1912, ii, 593).—Young beech leaves, without previous desiccation, were extracted with cold toluene and a resin, m. p. 62°, obtained, the properties of which were identical with those of the substance previously described (*loc. cit.*). Further investigations prove the presence of one ketonic and two carboxylic groups, one of which is free and the other esterified by the butyl radicle. The substance is therefore *n*-butyl hydrogen betularetinate, $\text{CO}_2\text{H}\cdot\text{C}_{34}\text{H}_{60}\text{O}\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9$. The free acid must therefore have the formula $\text{C}_{36}\text{H}_{62}\text{O}_5$, whereas Kosmann (*J. Pharm. Chim.*, 1854, [iii], 26, 197) gives $\text{C}_{36}\text{H}_{86}\text{O}_5$. It forms a reddish-yellow, transparent, brittle resin, readily soluble in alcoholic sodium hydroxide solution and the usual organic solvents, sparingly so in carbon tetrachloride. H. W.

Some Chemical Constituents of Green Plants. VIII. Detection of Formaldehyde in Plants. IX. Some Non-volatile, Water-soluble Constituents of the Leaves of the Edible Chestnut. T. CURTIUS and H. FRANZEN (*Sitz. Heidelberger Akad. Wiss. Math.-Nat. Kl. Abt., A.*, 1915, 8 pp.; *ibid.*, 1916, 18 pp.; from *Physiol. Abstr.*, 1917, 2, 194—195).—VIII. The authors correct their previous view that formaldehyde can be demonstrated by steam distillation of green leaves, and oxidation of the distillate with silver oxide, yielding formic acid. They now hold with Fincke that formaldehyde is absent, and that the formic acid was probably derived from methyl alcohol, which they find is oxidised to this acid by silver oxide. IX. The authors obtained, after purification with lead acetate, a greyish-brown, amorphous, pectin-like substance, a tannin, and *D*-inositol. G. B.

Fucose or Fucosan in *Fucus virsoides*. E. VOTOČEK and B. RÖHLICH (*Zeitsch. Zuckerind. Böhm.*, 1916, 41, 2—3).—*Fucus virsoides* from the coast at Abbazia, on the Gulf of Quarnero, was soaked first in water and then in 3% hydrochloric acid solution, the latter being removed by washing, and the purified seaweed then hydrolysed with 3% sulphuric acid solution. The resultant solution contained no galactose and little pentose, but a large proportion of fucose. T. H. P.

Methyl Nonyl Ketone from Palm Kernel Oil. ARTHUR HENRY SALWAY (T., 1917, 111, 407—410).—Before being employed in the production of foods, many vegetable oils have to be submitted to a process of steam distillation in order to remove small quantities of volatile substances, chiefly neutral oils, which are detrimental to the taste and odour of the articles. In the case of palm kernel oil, it is now reported that the chief obnoxious constituent is methyl nonyl ketone, of which there is about 0.1% in the crude oil. This ketone is also found in cocoanut oil, but methyl heptyl ketone and methyl undecyl ketone are present as well (compare Haller and Lassieur, A., 1910, i, 808). J. C. W.

The Proteolytic Enzymes of *Pinguicula vulgaris*. K. G. DERNBY (*Biochem. Zeitsch.*, 1917, 80, 152—158).—The dialysed expressed juice of *Pinguicula vulgaris* does not possess the property of thickening milk; it causes, however, a partial scission of milk caseinogen and of Witte's peptone when the reaction is neutral or faintly alkaline. The proteoclastic ferment causing the action is in many respects similar to trypsinogen, and the optimal hydrion concentration for its activity is about $p_H=8$. The juice contains no ereptic ferment (no action on glycylglycine), and no peptic ferment. S. B. S.

β -Galactosidase in the Vegetable Kingdom. MOUGNE (*J. Pharm. Chim.*, 1917, [vii], 15, 339—345).— β -Galactosidase was found to be present in the kernels of plums, peaches, apricots, and

cherries, in the seeds of apples, in the fresh leaves of the cherry laurel, of horse-radish and of aucuba, and in the seeds of *Sinapis alba* and *nigra*. Negative results were obtained with fresh kephir and *Aspergillus niger*. W. G.

The Biochemistry of Plants. A. STUTZER (*Biochem. Zeitsch.*, 1917, **80**, 143—151).—Attention is directed to the fact that certain plant diseases are apt to appear in soils of which the reaction is alkaline, and experiment with a mildew on roses indicates that the disease will disappear if the plant is transferred to a more favourable soil. An account is given by the author of the method for determining the acidity or alkalinity. The soil extract is treated with solutions of potassium iodide and iodate. In the presence of free acids, the reaction $\text{HIO}_3 + 5\text{HI} = 3\text{I}_2 + 3\text{H}_2\text{O}$ takes place, and the iodine set free is titrated with thiosulphate. In the case of alkaline soils, the extract is treated with standard acid, the titre of which against thiosulphate is known; the diminution of this titre gives the amount of alkali. Variations in the amount of acid and alkali are, however, found in the same sample of the soil, which depend on the ratio of the amount of water used for extraction to the amount of soil. S. B. S.

Isolation of Stachydrin from Lucerne Hay. H. STEENBOCK (*Proc. Amer. Soc. Biol. Chem.*, 1916, xxvii; *J. Biol. Chem.*, 1917, **29**).—The author has isolated *l*-stachydrin in the pure form, and as the hydrochloride, from the phosphotungstic acid fraction of the water-soluble constituents of lucerne hay. H. W. B.

Soil Solution. J. P. VAN ZYL (*J. Landw.*, 1916, **64**, 201—275).—Various methods of obtaining representative soil solutions were compared, and it was found that extraction by pressure gave the best results. Using this method, the soil from a particular field was studied in detail and samples were taken from a limed and from a dunged plot in summer and in winter. These were subjected to pressure and the solutions obtained were analysed; the concentration of the solutions varied according to both the manurial treatment and the season of the year, but the percentage composition of the ash remained constant, thus lending support to the Cameron-Whitney theory of soil solution.

The author points out that in order to get a true knowledge of the physical structure of a soil, its mechanical analysis should be carried out in its own soil solution. Comparative sedimentation tests were made, using distilled water and soil solution; when soil solution was employed the liquid cleared much more quickly, but fifteen washings only removed 2% of the clay; on the other hand, when distilled water was used, deflocculation was more complete and fifteen washings removed all the clay from the soil. Two series of mechanical analyses were then undertaken on the soil samples mentioned above (that is, limed and dunged plots in summer and winter); in one case distilled water was used and in the other soil solution. The results again showed evidence of the flocculating

action of the soil solution, so much so that the separation of the three finest fractions from one another was not attempted. These groups of three fractions (0.006 to 0.0005 mm.) were afterwards treated with distilled water and complete separation effected. It was found that the number of washings required for the operation varied from 80 to 120, was higher on the dunged plot than on the limed plot, and higher in winter than in summer. L. M. U.

Relation between Indications of Several Lime-requirement Methods and the Soil's Content of Bases. C. J. SCHOLLENBERGER (*Soil Sci.*, 1917, 3, 279—288).—Two soils were extracted with hydrochloric acid of various concentrations ranging from $N/100$ to $N/1$, and the free acid in the extracts was estimated by titration with $N/10$ -sodium hydroxide. From the results, the amount of bases removed from the soils in each case was calculated. When these extracted bases were plotted against the strength of the acid used, the curve rose sharply up to a certain point and then much more slowly; it would appear that all the more easily soluble bases in the soil were dissolved by $N/5$ -acid.

The residues from the extraction were then tested for lime requirement by the Hopkins, the Hutchinson-McLennan, and the vacuum methods, and it was found that the last gave results which corresponded best with the amount of base extracted.

The author suggests that the "total base-absorbing capacity" of a soil may be represented by adding the lime requirement as determined by the vacuum method to the amount of base extracted by $N/5$ -acid, and that the bases extracted by $N/5$ -acid may be taken as that part of the "base-absorbing capacity" which is already "satisfied." In this way, an expression can be obtained of the percentage of the total base-absorbing capacity or of the lime requirement which is still unsatisfied, and this may be used as a means of comparing the acidity or alkalinity of different soils. A series of pot cultures carried out to test this theory showed that the two neutral soils had more than 75% and the three alkaline soils 90% of their total base-absorbing capacity satisfied, whilst with all the acid soils the percentage was lower. L. M. U.

Organic Chemistry.

Preparation of Acetic Anhydride. H. DREYFUS (Brit. Pat., 100450, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 614).—In the preparation of acetic anhydride by the action of sulphur chlorides on sodium acetate, the evolution of sulphur dioxide and formation of chlorinated by-products may be avoided by: (a) using the reagents in the proportion of 6 atoms of chlorine to 8 acetyl groups; (b) employing a diluent such as acetic anhydride; (c) maintaining the temperature below 10–15°, and, preferably, below 0° until all the sulphur chloride has been added. Sulphur may be removed from the product by heating it with compounds of metals which form sulphides in the presence of acetic acid (such as the oxides or acetates of lead and copper), or it may be oxidised to sulphuric acid by permanganate, nitric acid, or nitrates. Thus, a mixture of dry powdered sodium acetate (720 kilos.) and acetic anhydride (600 kilos.) is cooled below 0° and sulphur dichloride (306 kilos.) is gradually introduced, the temperature being maintained at about 0° and the mixture being continually stirred. Stirring is continued for some time after the addition of sulphur dichloride is complete and the acetic anhydride is distilled off, preferably in a vacuum. The product is heated with a small quantity of copper oxide until free from sulphur. H. W.

Preparation of Acetic Anhydride. H. DREYFUS (Brit. Pat., 100452, addition to Brit. Pat., 100450, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 668).—In the process described in the original patent, the acetic anhydride should be distilled off in a vacuum at temperatures below 150°; otherwise, it is partly decomposed by the free sulphur with formation of acetic acid. H. W.

The Formation of Esters. D. McINTOSH (*J. Amer. Chem. Soc.*, 1917, **39**, 1073–1074. Compare A., 1906, i, 481; Kendall and Booge, A., 1916, i, 707).—A very brief summary of work in progress. The freezing-point curves of systems such as methyl alcohol-acetic acid show no indication of the formation of compounds, but methyl or ethyl alcohol forms compounds with strong acids such as hydrobromic acid (compare Baume, A., 1912, ii, 329). Similar compounds are formed by acetic acid or its esters. Equimolecular mixtures of acetic acid and the alcohols apparently yield compounds with hydrobromic acid. At low temperatures there is no indication of ester formation. W. G.

Synthesis of $\alpha\beta$ -Thiocrotonic Acid. PRAFULLA CHANDRA RÂY and MANIK LAL DEY (T., 1917, **111**, 510–512).—A solution of molecular proportions of thioacetamide and monochloroacetic acid in acetone gradually deposited ammonium chloride with simultaneous formation of $\alpha\beta$ -thiocrotonic acid, $\text{CMe} \searrow \text{C} \cdot \text{CO}_2\text{H}$, which

was further converted into its barium, lead, and silver salts and a

chloromercuri-derivative, $\begin{array}{c} \text{CMe:C—CO} \\ \diagdown \quad \diagup \\ \text{S} \cdot \text{HgCl} \end{array}$. The acid was reduced by

hydriodic acid to β -iodo- $\alpha\beta$ -thiobutyric acid, $\begin{array}{c} \text{CMeI} \\ \diagdown \quad \diagup \\ \text{S} \end{array} \text{CH} \cdot \text{CO}_2\text{H}$,

which was isolated in the form of its silver salt. In accordance with the general rule, $\alpha\beta$ -thiocrotonic acid possesses a higher dissociation constant than its sulphur-free analogue crotonic acid.

For details the original should be consulted.

D. F. T.

Incomplete Hydrogenation of Cotton-seed Oil. HUGH K. MOORE, G. A. RICHTER, and W. B. VAN ARSDEL (*J. Ind. Eng. Chem.*, 1917, 9, 451—462).—An investigation of the changes in the amount, character, and chemical characteristics of the glycerides in oils during hydrogenation, and the changes in the properties of the oils themselves as regards saponification value, melting point, the response to the Halphen test, etc. The changes in the composition and the oil constants are expressed graphically, and the paper is illustrated with curves and diagrams. The conditions of hydrogenation, such as pressure, temperature, percentage of catalyst, and the degree of agitation were shown to affect the proportions of saturated glycerides, olein, and linolein in partially hydrogenised cotton-seed oil, and the effect of these variables on the velocity of hydrogenation was studied by means of iodine number-time curves. The increase in velocity is roughly proportional to the increase in pressure or amount of catalyst, whilst increase in temperature of 10° between 160° and 180° increases the rate by only about 20%. The change in the melting point of the oil and its fatty acids during hydrogenation was also followed by iodine number curves, and the latter was found to pass through a minimum before beginning to increase. The degree of hydrogenation necessary to destroy the response of cotton-seed oil to the Halphen test corresponds with a drop of about four units in the iodine number. Experiments on the influence of certain inorganic materials on the catalyst showed that whilst sodium chloride, nitrate, and sulphate, nickel chloride, and reduced iron had no effect, sodium sulphide, sulphur, chlorine, sulphur dioxide, hydrogen sulphide, or water vapour in the hydrogen destroyed the activity of the catalyst.

G. F. M.

Preparation of Deoxycholic Acid. WILLIAM MAIR (*Biochem. J.*, 1917, 11, 11—13. Compare Wieland and Sorge, A., 1916, i, 710).—Deoxycholic acid has a remarkably intense solvent action on pneumococci. It is prepared with maximum yield from ox bile by prolonged boiling with sodium hydroxide and subsequent neutralisation with hydrochloric acid. After filtration, the acid is thrown down by acetic acid and purified by several recrystallisations from 60% acetic acid. The yield of pure deoxycholic acid is about 10 grams from a litre of bile.

H. W. B.

Synthesis of Hæmatic Acid and the Oxidation of Hæmatin.

WILLIAM KÜSTER and JOHANNES WELLER (*Zeitsch. physiol. Chem.*, 1917, **99**, 229—254. Compare A., 1914, i, 442).—A detailed description of work previously published.

Ethyl α -acetylglutarate, $C_{11}H_{18}O_5$, prepared from ethyl acetate and ethyl iodopropionate by the action of sodium, is a colourless oil, b. p. 169—171°/22—25 mm.

Racemic *β -hydroxypentane- $\beta\gamma$ -tricarboxylic acid*, $C_8H_{12}O_7$, crystallises with $1H_2O$ and has m. p. 108—110°.

The lactone of the above acid on heating yields, besides methyl-ethylmaleic anhydride, a small amount of a crystalline substance which appears to be a derivative of itaconic acid, empirical formula, $C_7H_{10}O_4$, m. p. usually 179—180° (decomp.), but varies with rate of heating. The same compound is formed by heating hæmatic acid.

Varying yields of hydroxy-acids are obtained by oxidising hæmatin with various oxidising agents. H. W. B.

Compounds of Calcium Chloride and Acetone.

LANCELOT SALISBURY BAGSTER (T., 1917, **111**, 494—497).—Calcium chloride combines with acetone to form two compounds, which, according to vapour pressure measurements, have the composition $CaCl_2 \cdot 2C_3H_6O$ and $CaCl_2 \cdot C_3H_6O$ respectively. The dissociation pressures of the compounds have been determined at temperatures between 20° and 64°. H. M. D.

Preparation of Ketones.

G. SCHICHT and A. GRÜN (D.R.-P., 295657; from *J. Soc. Chem. Ind.*, 1917, **36**, 569—570).—Ketones may be prepared by heating monocarboxylic acids of b. p. above 300° in the liquid state to temperatures not greatly exceeding 300° with small quantities of ketone-producing catalysts (finely-divided metals, oxides, silicates, or silicic acid). Mixtures of catalysts, or catalysts deposited on finely-divided carriers or on filtering material, may be employed. In consequence of the relatively low temperature of the reaction and the absence of energetic reagents, the yield is practically quantitative. Stearic acid yields stearone, $CO(C_{17}H_{35})_2$, m. p. 87°. Commercial stearin, m. p. 54°, gives a mixture of stearone, palmitone, and stearopalmitone, m. p. 75°. H. W.

Preparation of Ketones.

G. SCHICHT and A. GRÜN (D.R. P., 296677; addition to D.R.-P. 295657; from *J. Soc. Chem. Ind.*, 1917, **36**, 615. Compare preceding abstract).—Monocarboxylic acids of b. p. above 300° are heated in the liquid state in iron vessels without the addition of catalysts. Thus technically pure stearic acid, m. p. 68°, gives a quantitative yield of technically pure stearone, m. p. 84·6°, free from acid, when heated for three hours at 295°. It is not necessary to provide for the continuous removal of carbon dioxide and water as might be expected; the operation is preferably carried out in an autoclave. H. W.

The Preparation of Xylose. C. S. HUDSON and T. S. HARDING (*J. Amer. Chem. Soc.*, 1917, **39**, 1038—1040).—An 8—12% yield of xylose can be obtained from cotton-seed hulls by direct acid hydrolysis. The hulls are first left in contact with 2% ammonium hydroxide for twelve hours and then boiled with 7% sulphuric acid for two hours. The hulls are strained off and the liquid neutralised with calcium hydroxide. The calcium sulphate is filtered off, the filtrate decolorised with charcoal, and concentrated under reduced pressure. Alcohol is added, and the liquid, after filtration, is further concentrated to a syrup, from which by suitable treatment with alcohol the xylose is obtained in a crystalline form. W. G.

Sedoheptose, a New Sugar from *Sedum spectabile*. I. F. B. LA FORGE and C. S. HUDSON (*J. Biol. Chem.*, 1917, **30**, 61—77).—An aqueous extract of the leaves and stems of one of the stonecrops, *Sedum spectabile*, contains a non-fermentable, reducing sugar, *sedoheptose*, $C_7H_{14}O_7$, which has been obtained in the form of a dextro-rotatory syrup. When treated with phenylhydrazine, it yields a *phenylosazone*, $C_{19}H_{24}O_5N_4$, m. p. 197° (decomp.). The corresponding *p*-bromophenylosazone, $C_{19}H_{23}O_5N_4Br_2$, crystallises in bright yellow needles from methyl alcohol, m. p. 227—228° (decomp.). The *osone*, prepared in the usual way, does not crystallise readily, but its *o*-phenylenediamine derivative, $C_{13}H_{16}O_5N_2$, is deposited in long, white needles after the addition of a hot aqueous solution of *o*-phenylenediamine to the osone syrup. It crystallises with $\frac{1}{2}H_2O$ and melts at 163—165°.

By the reduction of a solution of the sugar from the plant extract with sodium amalgam, two heptahydric alcohols are produced. *α -Sedoheptitol*, $C_7H_{16}O_7$, has m. p. 151—152° and $[\alpha]_D^{20} + 2.25^\circ$, and when dissolved in 50% sulphuric acid and treated with benzaldehyde it yields *tribenzylidene- α -sedoheptitol*, $C_{28}H_{28}O_7$, m. p. 199—200°. From the syrupy residue after the separation of *α -sedoheptitol*, a second benzaldehyde compound is isolated which is found to be *tribenzylidene- β -sedoheptitol*, $C_{28}H_{28}O_7$, crystallising from methyl ethyl ketone in tufts of flexible needles resembling asbestos, m. p. 272—275°. On hydrolysis, the free optically inactive *β -sedoheptitol*, $C_7H_{16}O_7$, is obtained, prisms, m. p. 127—128°.

On heating the plant extract with dilute acid, it loses about 80% of its reducing power towards Fehling's solution. When the extract which has been heated with acid is treated with benzaldehyde, a crystalline compound is obtained which proves to be the benzylidene derivative of a heptose which has lost one molecule of water. *Dibenzylideneanhydrosedoheptose*, $C_{21}H_{20}O_6$, is insoluble in most of the usual solvents, but crystallises from hot acetic anhydride in long white prisms, m. p. 245°. On hydrolysis, the crystalline anhydride is obtained. *Anhydrosedoheptose*, $C_7H_{12}O_6$, m. p. 155°, $[\alpha]_D^{20} - 146.3^\circ$ without mutarotation, does not reduce Fehling's solution, but on heating with dilute acid, it passes to the extent of about 20% into *sedoheptose*. Since boiling the original syrup containing *sedoheptose* with dilute acid diminishes the reducing power until it is about 20% of that originally ob-

served, it follows that mutual transformation of these two substances occurs in acid solution until equilibrium is established, when the solution contains 20% of sedoheptose and 80% of anhydrosedoheptose.

Sedoheptose is probably a ketose, because bromine does not oxidise it, and the two alcohols mentioned above result from its reduction.

H. W. B.

Indirect Measurements of the Rotatory Powers of some α - and β -Forms of the Sugars by Means of Solubility Experiments. C. S. HUDSON and E. YANOVSKY (*J. Amer. Chem. Soc.*, 1917, **39**, 1013—1038).—In order to test the suggestion previously made by Hudson (compare A., 1909, i, 135) that the difference between the molecular rotations of the α - and β -forms of the sugars showing mutarotation is a constant quantity, the authors have determined the rotations of the unknown forms of the mutarotating sugars by the method previously described for lactose (compare Hudson, A., 1904, i, 974; Lowry, T., 1904, **85**, 1551). This depends on the measurement of the maximum rate of solution of the corresponding known isomeride or of its initial and final solubility. It is now shown that these mutarotating sugars have another common property, namely, a measurable maximum rate of solution, which is caused by the slow establishment in solution of equilibrium between the α - and β -forms. Sugars showing no mutarotation do not give this maximum rate of solution. The values obtained for the specific rotations of the α - and β -forms in water at 20° and the velocity coefficients of the mutarotation of the sugars examined are:

Sugar.	Specific rotation in water.			Velocity coefficients of mutarotation.
	α -form.	Constant rotation.	β -form.	
<i>d</i> -Glucose	+113.4°	+52.2°	+19.0°	0.0065
<i>d</i> -Galactose	+144.0	+80.5	+52.0	0.0102
<i>d</i> -Mannose	+34.0	+14.6	-17.0	0.0190
<i>d</i> -Fructose	-21.0	-92.0	-133.5	0.082
<i>d</i> -Xylose	+92.0	+19.0	-20.0	0.021
<i>d</i> -Lyxose	+5.5	-14.0	-36.0	0.065
<i>d</i> -Arabinose.....	-54.0	-105.0	-175.0	0.031
<i>l</i> -Rhamnose.....	-7.7	+8.9	+54.0	0.039
α -Glucoheptose..	+45.0	-20.4	-28.4	0.0123
Lactose	+90.0	+55.3	+35.0	0.0046
Maltose.....	+168.0	+136.0	+118.0	0.0072
Melibiose	+179.0	+142.5	+124.0	0.0088
Cellose	+72.0	+35.0	+16.0	0.0047

The highest value previously recorded for the specific rotation of α -glucose is 110° (compare Hudson and Dale, this vol., i, 320), but the specimen prepared for this work had $[\alpha]_D^{20} +113.4^\circ$ in water, $+115.2^\circ$ in 80% alcohol, and $+121.5^\circ$ in absolute methyl alcohol.

The results obtained show fairly constant differences between the molecular rotations of the α - and β -forms, except in the case of mannose, lyxose, and rhamnose. It is possible that the exceptional difference for these sugars may be dependent on a configurational

type, since the configurations of these three sugars are identical from the γ -carbon atom upwards.

The initial and final solubilities of most of the crystalline sugars in various strengths of alcohol are tabulated in the original.

W. G.

The Preparation of β -Glucose. A. W. MANGAM and S. F. ACREE (*J. Amer. Chem. Soc.*, 1917, **39**, 965—968).—The authors find that Behrend's method for the preparation of β -glucose (compare A., 1911, i, 14) by crystallisation of α -glucose from pyridine is satisfactory. The product is best dried at 105° or in a vacuum desiccator over sulphuric acid.

W. G.

The Rotatory Powers of some New Derivatives of Gentiobiose. C. S. HUDSON and J. M. JOHNSON (*J. Amer. Chem. Soc.*, 1917, **39**, 1272—1277).—By a modification of Zemplén's process (A., 1913, i, 707), the authors have obtained a greatly increased yield of gentiobiose octa-acetate (m. p. $192\text{--}193^\circ$, $[\alpha]_D^{20} - 5.3^\circ$) from commercial gentian root. This octa-acetate when heated in acetic anhydride containing a little zinc chloride undergoes transformation into an *isomeride*, m. p. $188\text{--}189^\circ$, $[\alpha]_D^{20} + 52.3^\circ$ (in chloroform). It has already been shown that the α - and β -octa-acetates of maltose, lactose, and cellose in each case differ in specific rotation by approximately 57° , and in accordance with this result Zemplén's octa-acetate must be regarded as the β -compound and the new isomeride as the α -compound.

β -Gentiobiose octa-acetate, by the action of an acetic acid solution of hydrogen bromide, was converted into the syrupy bromohepta-acetyl compound, which on treatment with silver carbonate in methyl alcoholic solution gave β -hepta-acetylmethylgentiobioside, $C_{12}H_{14}O_{10}Ac \cdot OMe$, m. p. 82° , $[\alpha]_D^{20} - 18.8^\circ$ in chloroform, this rotatory power agreeing approximately with the value calculated from the molecular rotation of the acetylated gentiobiose chain and of the lactonyl carbon of the acetylated methyl glucosides. Hydrolysis of the last product with aqueous barium hydroxide yielded β -methyl gentiobioside, $C_{12}H_{21}O_{10}OMe$, m. p. 96° , $[\alpha]_D^{20} - 36.0^\circ$ in water, this rotatory power also approximating to that expected from the values for the gentiobiose chain and the asymmetric lactonyl carbon atom of the methyl glucosides.

D. F. T

Action of Formaldehyde on Lactose, Maltose, and Sucrose. A. HEIDUSCHKA and H. ZIRKEL (*Arch. Pharm.*, 1916, **254**, 456—487).—The observations recorded in the literature of the action of formaldehyde on different kinds of sugars are so contradictory that a further study of the subject appears desirable. The authors have examined the substances obtained from formaldehyde and lactose, maltose, or sucrose in aqueous solution. Formaldehyde and the biose yield products the compositions of which vary with the relative proportions of the sugar and formaldehyde used in the preparation, and any one product does not differ in essential chemical characteristics from any other product or from its com-

ponents. The products therefore are not to be regarded as definite chemical compounds. Products containing up to 39% of formaldehyde have been prepared; from products containing a higher percentage paraformaldehyde separates. Products containing a high percentage of formaldehyde yield products containing a lower percentage by evaporating their aqueous solution in a vacuum. The capacity to take up formaldehyde is different in the three bioeses, being greatest in sucrose and least in maltose. The formaldehyde in the products can be estimated by the sulphite method and the sugar polarimetrically, the sum of the two percentages being 100.

Following the directions of Oppermann and Goehde (Brit. Pat., 6653 of 1897) and of Rosenberg (A., 1908, i, 320), the authors have been unable to obtain from lactose and formaldehyde substances having the compositions recorded by these investigators. The products lose all their formaldehyde at 190° and leave pure lactose. The products are soluble in alcohol. This is noteworthy since lactose is practically insoluble in this solvent. The authors now find, however, that lactose is more soluble in alcohol containing formaldehyde than in alcohol alone, and that the products mentioned above are more soluble in alcohol the greater is their formaldehyde content; from such solutions lactose is deposited almost quantitatively as the formaldehyde progressively reacts with the solvent.

Other properties of sugar and formaldehyde solutions, such as the density and the viscosity, have been examined, and the authors are of opinion that the products obtained from formaldehyde and a bioese are solid solutions of formaldehyde in the sugar. Since the sugar takes up relatively more formaldehyde from dilute solutions of formaldehyde than from concentrated solutions, adsorption processes would appear to be operative were it not that van Bemmelen's adsorption formula ($C_w^n/C_s = k$) is found not to hold.

C. S.

The Reaction between Starch and Formaldehyde, and the Diastatic Properties of Formaldehyde. GERTRUD WOKER (*Ber.*, 1917, 50, 679—692. Compare this vol., i, 61).—Polemical. A reply to von Kaufmann (this vol., i, 251) and a criticism of his experiments. In this, and in her first communication, the writer continually refers to experiments conducted by her colleague, Maggi, the details of which are to be published in another place. Apparently, a knowledge of these would have prevented confused criticism, for, as the following summary indicates, formaldehyde does somewhat resemble diastase in its behaviour towards starch.

(1) The microscopic appearance of the attack on starch granules by diastase and formaldehyde is the same. If the preparations are stained with iodine, a mosaic of blue, violet, red, brown, and yellow granules, representing unchanged starch and various dextrans, is obtained in each case. (2) Formaldehyde and diastase both liquefy starch. (3) Solutions of starch with diastase or formaldehyde behave towards iodine like mixtures of starch and achroo- and erythro-dextrans. (4) On dialysing the mixture of

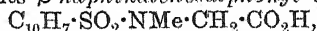
starch and formaldehyde, the residue reacts like a mixture of starch and dextrans, and the dialysate like a solution of lower dextrans, and even sugars, with formaldehyde. (5) The viscosity of a solution of starch and formaldehyde or diastase is lower than the mean viscosity of the constituents. (6) The freezing points of such mixtures are also lower than the mean. (7) Solutions of starch, glycogen, or dextrin and formaldehyde respond to the Moore-Heller reaction when sufficient alkali to destroy the formaldehyde is added, and they also give the typical caramel-like odour when treated with concentrated sulphuric acid. (8) Solutions of starch or dextrin and formaldehyde respond to Rubner's reaction if the formaldehyde is boiled away. (9) Mixtures of starch and formaldehyde have a greater reducing power towards Fehling's and Pavy's solutions than solutions containing the same amount of the aldehyde alone.

J. C. W.

Compounds of Amino-acids and Ammonia. IX. PETER BERGELL (*Zeitsch. physiol. Chem.*, 1917, **99**, 150—160. Compare A., 1916, i, 713).—Hydrolysis of iminodiacetamide with excess of sodium hydroxide yields iminodiacetic acid, which is isolated by means of its β -naphthalenesulphonyl derivative, already described (Bergell and Feigl, A., 1908, i, 396). The intermediate monoamide is obtained by subjecting iminodiacetamide to the action of the enzymes contained in the fresh liver of a mouse. The β -naphthalenesulphonyl derivative of the monoamide of iminodiacetic acid, $C_{10}H_7 \cdot SO_2 \cdot N(CH_2 \cdot CO \cdot NH_2) \cdot CH_2 \cdot CO_2H$, crystallises in rosettes of plates, m. p. 202—204° (decomp.).

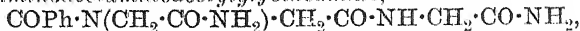
Benzoyliminodiacetamide gives off one molecule of ammonia when boiled with weak alkali hydroxide, leaving the *monoamide* of benzoyliminodiacetic acid, $C_{11}H_{12}O_4N_2$, prismatic needles, m. p. 190—191°.

Sarcosine may be readily recognised and isolated from its solutions by means of its β -naphthalenesulphonyl derivative,



which is prepared in the usual way, and crystallises in long needles from alcohol, m. p. 169—171°.

Glycineamide reacts with chloroacetylglycineamide, forming a derivative of iminodiacetic acid, which on benzoylation gives *benzoyliminodiacetamidoacetylglycineamide*,



crystallising with $1H_2O$ in prisms from alcohol, m. p. 186—188°.

H. W. B.

The Constitution of Cyanamide. EMILE COLSON (T., 1917, **111**, 554—561).—The densities and refractive indices of cyanamide and diethylcyanamide have been determined at 48°. The molecular refractivities, calculated according to the Lorenz-Lorentz formula, are compared with the corresponding numbers obtained by Brühl for dipropylcyanamide, diisamylecyanamide, and carbo-dipropylimide. The refractivity of the CN_2 group is obtained by subtracting from the above molecular refractivities the values of the refractivity of the contained hydrogen atoms or alkyl groups.

The refractivity of the CN_2 group in cyanamide, diethyl-, dipropyl-, and diisoamyl-cyanamide is thus found to be equal to about 8, whilst the refractivity of this group in carbodipropylimide is about 10. The structure of cyanamide is therefore in accordance with the formula $\text{N}:\text{C}:\text{NH}_2$.

The data are also discussed in relation to the atomic refractive power of nitrogen in the cyanamides. H. M. D.

Formation of Guanidine from Thiocarbamide and from Cyanamide. ERNST SCHMIDT (*Arch. Pharm.*, 1916, 254, 626—632).—Schenk has shown (A., 1911, i, 842; 1912, i, 685) that alkylated guanidines are obtained by desulphurising alkylated thiocarbamides in ammoniacal solution or in the presence of amines. The author now finds that, contrary to the old statement of Hofmann, dicyanodiamide is not the only product obtained when thiocarbamide in aqueous or aqueous-alcoholic ammonia solution is treated with yellow mercuric oxide for twenty-four hours at the ordinary temperature, guanidine also being produced, although not in large quantities. Cyanamide is first formed, which then mainly polymerises to dicyanodiamide, but also reacts with ammonia to some extent to form guanidine.

The same two changes occur when a solution of cyanamide, prepared by very faintly acidifying a solution of sodium cyanamide with 98% formic acid, is treated with mercuric oxide and aqueous ammonia as above, but the quantity of guanidine formed is somewhat larger and becomes considerably greater when the reaction is effected in a sealed tube at 100° . C. S.

The Crystal Form and Isomerism of some Ferrocyanides.

GEORGE MACDONALD BENNETT (T., 1917, 111, 490—494).—Crystallographic measurements of crystals of sodium ferrocyanide with an unusual development of faces are recorded and compared with previous data. Some of the crystals were found to be interpenetrative twins.

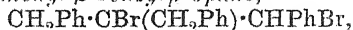
In connexion with this examination, the author prepared the α - and β -forms of sodium and potassium ferrocyanides and of the double salt formed by ammonium ferrocyanide with ammonium chloride (Briggs, T., 1911, 99, 1019). Goniometric measurements of the two forms showed that in all three cases they are crystallographically identical. The differences in colour, density, and solubility of the two forms, which are adduced by Briggs in support of the view that the two forms are stereoisomeric, are attributed to traces of impurities and to errors in the measurement of the density and the solubility. The marked difference in the optical rotatory powers of alcoholic solutions supposed to contain *L*-menthylamine α - and β -ferrocyanides respectively remains unexplained, but it cannot be attributed to the existence of isomeric forms.

Other pairs of salts supposed to represent stereoisomeric forms are also crystallographically identical according to goniometric data. H. M. D.

Aromatic Hydrocarbons from the Thermal Decomposition of Natural Gas Condensate. J. E. ZANETTI and G. EGLOFF (*J. Ind. Eng. Chem.*, 1917, **9**, 474—478).—The tar obtained by the thermal decomposition of natural gas condensates at temperatures above 750° by the methods previously described (A., 1916, i, 625, 705) was further investigated. It gave on distillation to 170°, 9.7%; to 230°, 18.7%; to 270°, 11.4%; to 330°, 15.1%, and a residue, 30.1%. In addition, a further 1.0—1.5 c.c. of light oil per cubic foot of gas used was scrubbed out of the gaseous product. From the above fractions the following substances were isolated: benzene, toluene, naphthalene, acenaphthene, anthracene, phenanthrene, pyrene, and chrysene. The apparatus employed for the decomposition of the condensate is illustrated in the paper, and is essentially the same as that already described, with the addition of a Cottrell separator to precipitate the tar "fog."
G. F. M.

Syntheses in the Indene Series. II. Synthesis of Diphenylindene. A. P. ORECHOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1702—1712).—The compound, m. p. 177—178°, previously regarded as 2:3-diphenylindene (A., 1914, i, 265), is not identical with the compound, m. p. 108—109°, similarly designated by Thiele and Ruggli (A., 1912, i, 866). These two compounds yield the same oxime when treated with amyl nitrite and sodium ethoxide, and both give 2:3-diphenyl-1-benzylideneindene when condensed with benzaldehyde in presence of potassium hydroxide. These results are explained on the assumption that the diphenylindene, m. p. 177—178°, is the 1:2-compound, which readily undergoes isomerisation into the 2:3-compound, m. p. 108—109°, under the influence of alkali. The remainder of this paper has been already published (*loc. cit.*).
T. H. P.

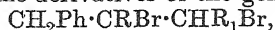
Syntheses in the Indene Series. III. Synthesis of Phenylbenzylindene. A. P. ORECHOV and (Mlle.) R. GRINBERG (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1713—1724. Compare preceding abstract).—Dehydration of tribenzylcarbinol by treatment with acetyl chloride yields β -phenyl- $\alpha\alpha$ -dibenzylethylene [$\alpha\gamma$ -diphenyl- β -benzylidenepropane], $\text{CHPh}\cdot\text{C}(\text{CH}_2\text{Ph})_2$, which forms an almost colourless, highly viscous liquid, b. p. 231—232°/11 mm., exhibits normal cryoscopic behaviour in benzene, and instantly decolorises a chloroform solution of bromine.
 $\alpha\beta$ -Dibromo- $\alpha\gamma$ -diphenyl- β -benzylpropane,



forms colourless needles, m. p. 127—128°, and has the normal molecular weight in freezing benzene. When heated in an oil-bath at 150—155°, this compound loses hydrogen bromide, giving 3-phenyl-2-benzylindene, $\text{C}_6\text{H}_4\langle\text{CH}_2\text{CPh}\rangle\text{C}\cdot\text{CH}_2\text{Ph}$, which crystallises in hard, colourless prisms, m. p. 92—93°, exhibits normal cryoscopic behaviour in benzene, and decolorises bromine in chloroform solution. Like indene derivatives in general, 3-phenyl-2-benzyl-

indene condenses with benzaldehyde in presence of alcoholic potassium hydroxide, yielding 3-phenyl-2-benzyl-1-benzylidene-indene, $C_6H_4 \langle \begin{smallmatrix} C:(CHPh) \\ \text{---} \\ CPh \end{smallmatrix} \rangle C \cdot CH_2Ph$, which forms small, golden-yellow needles, m. p. 174—175°.

In all the cases which have now been investigated of ring-formation with dibromo-derivatives of the general type

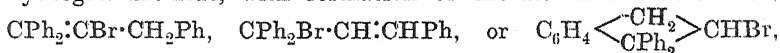


no hydrogen is attached to the second carbon atom of the propane chain, so that elimination as hydrogen bromide of the bromine atom united to the third carbon atom cannot occur otherwise than by ring-closure. The method is therefore now being extended to dibromo-compounds with which this condition does not hold, namely, $\alpha\beta$ -dibromo- $\alpha\gamma$ -triphenylpropane, $\alpha\beta$ -dibromo- $\alpha\gamma$ -diphenylpropane, and $\alpha\beta$ -dibromo- γ -phenylpropane. These investigations are still incomplete, but the following compounds have been prepared.

$\alpha\gamma$ -Triphenylpropan- α -ol, $CH_2Ph \cdot CH_2 \cdot CPh_2 \cdot OH$, obtained by the action of magnesium phenyl bromide on ethyl β -phenylpropionate, forms long, slender, colourless needles, m. p. 87—88°, and in concentrated sulphuric acid gives an intense orange-yellow solution rapidly becoming pale yellow.

$\alpha\gamma$ -Triphenyl- Δ^2 -propene, $CH_2Ph \cdot CH : CPh_2$, prepared by the dehydration of $\alpha\gamma$ -triphenylpropan- α -ol by means of acetyl chloride or hydrogen chloride, forms a pale yellow, viscous oil, b. p. 229—230°/17 mm.

This olefinic hydrocarbon readily combines with two atoms of bromine. The dibromo-compound is a yellow, viscous oil which could not be crystallised; when boiled with acetic acid, it loses hydrogen bromide, with formation of the monobromo-derivative,



which crystallises in very long, thin needles, m. p. 98—99°, and has the normal molecular weight in freezing benzene. The product obtained on heating the monobromo-derivative with alcoholic potassium hydroxide appears to be a mixture of the hydrocarbon, $C_{21}H_{16}$, with the compound $C_{21}H_{17} \cdot OH$ or $C_{21}H_{17} \cdot OEt$. T. H. P.

Separation of Secondary Arylamines from Primary Amines. JOHN THOMAS (T., 1917, 111, 562—572).—Although primary aromatic amines react readily with ethyl oxalate, producing a mixture of a substituted oxamic ester and a substituted oxamide, secondary aromatic amines, for example, ethyl-*o*-toluidine, ethylaniline, and methylaniline, react very little under the same conditions. This difference in behaviour can therefore be applied to the separation of primary and secondary aromatic amines; if the b. p. of the ester is inconveniently close to that of the secondary amine, butyl oxalate can be used instead of ethyl oxalate.

For details of the effect of variation in the conditions of treatment see the original paper.

D. F. T.

Groups of Bases Obtained from Aromatic Amines and Formaldehyde. ROBERTO LEFETIT and CARLO MAIMERI (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 558—563. Compare this vol., i, 197, 198).—The authors have repeated Goldschmidt's work (A., 1898, i, 184) on the action of formaldehyde on *p*-phenetidine hydrochloride, the resultant products comprising the four bases: (1) methyl-*p*-phenetidine, b. p. 102—104°/4 mm.; (2) a base, m. p. 146—147°, obtained in small proportion and not investigated; (3) a base, $C_{18}H_{20}O_2N_2$, m. p. 140°, identical with that to which Goldschmidt ascribed the formula $C_{18}H_{22}O_2N_2$. The accuracy of the formulæ now suggested is shown by the compositions of the corresponding bases given under similar conditions by *p*-anisidine and *p*-toluidine, namely, $C_{16}H_{16}O_2N_2$ and $C_{16}H_{16}N_2$, respectively. (4) A base, forming a bitter, anæsthetic hydrochloride, to be described later. T. H. P.

Chemical Composition of the Higher Fractions of Maplewood Creosote. ERNEST J. PIEPER, S. F. ACREE and C. J. HUMPHREY (*J. Ind. Eng. Chem.*, 1917, **9**, 462—465).—The fractional distillation of maplewood creosote gave 75% of wood creosote and 25% of pitch. Of the former, 14% boiled at 93—195°, 31% at 195—230°, and 55% at 230—280°. The lower fractions consisted mainly of guaiacol and creosol, whilst the various fractions of creosote oil above 195° on extraction with alkali gave 15—25% of neutral oil, the residue being phenols, the sodium salts of which separated out from the alkaline solution. From the mixed salts benzoyl derivatives and oxidation products were prepared, and the presence of pyrogallol dimethyl ether, methylpyrogallol dimethyl ether, and propylpyrogallol dimethyl ether in the original creosote fractions was thus established. These constituents are identical with those found in beechwood creosote, but differ in the amounts present. G. F. M.

Analogies between Derivatives of Oxygen and those of Nitrogen. II. A. ANGELI (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 480—484. Compare A., 1910, ii, 844, 948; Diels and Paquin, A., 1913, i, 839).—The analogy between hydrogen peroxide, hydroxylamine, and hydrazine is also shown by quinol, *p*-amino-phenol, and *p*-phenylenediamine. Thus, on oxidation, the former compounds yield respectively O:O, O:NH, and NH:NH, the last two of these being highly unstable and exhibiting a marked tendency to polymerise and decompose: $2NH:O \rightarrow OH:N:N:OH \rightarrow N_2O + H_2O$ and $2NH:NH \rightarrow NH_2:N:N:NH_2 \rightarrow N_3H + NH_3$. Similarly, oxidation of the above benzene derivatives gives *p*-benzoquinone, *p*-benzoquinoneimine, and *p*-benzoquinonedi-imine; further, *p*-benzoquinoneimine yields a polymeride of unknown constitution, and *o*-benzoquinonedi-imine readily furnishes *o*-azoaniline.

Dimethylamine yields nitrosoamine when treated with nitrous acid, and dimethylaniline behaves similarly. Nitroethane gives methylnitrolic acid and *p*-nitrotoluene yields *p*-nitrobenzaldehyde. The formation of formic acid from chloroform and alkali

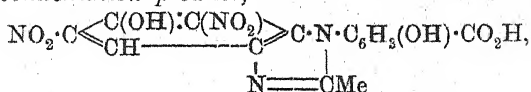
is analogous to Tiemann's synthesis of aromatic hydroxy-aldehydes. The transformation, $2\text{CH}_3\text{Me}\cdot\text{NO}_2 \rightarrow \text{NO}_2\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{NO}_2$, corresponds with $2\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2 \rightarrow \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$.
T. H. P.

Preparation of Acyl Derivatives of 6-Amino- α -naphthol-3-sulphonic Acid. CHEMISCHE FABRIK GRIESHEIM ELEKTRON (D.R.-P., 295767; from *J. Soc. Chem. Ind.*, 1917, **36**, 542).—Acyl derivatives of 6-amino- α -naphthol-3-sulphonic acid are prepared by condensing 3-hydroxy- β -naphthoic acid haloids, or the O-acetyl compounds, with 6-amino- α -naphthol-3-sulphonic acid. The products have strong affinity for cotton and silk. 3-Hydroxy- β -naphthoyl-6-amino- α -naphthol-3-sulphonic acid gives in alkaline solution the typical yellow colour of the 3-hydroxy- β -naphthoic acid arylamino-alkali salts. It combines with two molecules of diazo-compound and is absorbed by cotton from alkaline solutions and by silk from acetic acid solutions. Valuable colours, fast to washing, are obtained by treating the fabrics with diazo-compounds. H. W.

Condensation, under the Influence of Potassium Hydroxide, of cycloHexanol with isoPropyl Alcohol; Synthesis of cycloHexylisopropyl Alcohol. MARCEL GUERBET (*Compt. rend.*, 1917, **164**, 952—954).—cycloHexanol and isopropyl alcohol, when heated in sealed tubes at 220° for twenty-four hours in the presence of anhydrous potassium hydroxide, undergo condensation, giving γ -cyclohexylisopropyl alcohol, $\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, a colourless alcohol, b. p. $204\text{--}205^\circ/764$ mm. (corr.); D_0 0.9203, which forms an acetate, b. p. $213\text{--}214^\circ/763$ mm. (corr.), and a phenylcarbamate, prismatic needles, m. p. $124\text{--}125^\circ$. The alcohol when oxidised with chromic acid yields cyclohexylacetone [cyclohexylmethyl methyl ketone], b. p. $194\text{--}195^\circ/761$ mm. (corr.); D_0 0.9350, giving a crystalline compound with sodium hydrogen sulphite, and a semicarbazone, m. p. $199\text{--}200^\circ$. On further oxidation, the ketone gives acetic and cyclohexanecarboxylic acids. W. G.

Attempts to Prepare Asymmetric Quinquevalent Nitrogen Compounds. I. 5-Aminosalicyclic Acid and Related Compounds. RAPHAEL MELDOLA, HENRY STENNETT FOSTER, and RAINALD BRIGHTMAN (*T.*, 1917, **111**, 533—546).—A preliminary investigation of 5-aminosalicylic acid and its derivatives with a view to the later production of derived quinone-ammonium compounds containing an asymmetric nitrogen atom.

5-Aminosalicyclic acid resisted attempts at methylation, but was convertible into 5-dibenzylaminosalicylic acid, $\text{C}_{21}\text{H}_{19}\text{O}_3\text{N}$, which on subsequent methylation yielded 2-carboxy-4-dibenzylmethylammonium-1-benzoquinone, $\text{O}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{NMe}(\text{C}_7\text{H}_7)_2$. It reacted readily with 2:3:6-trinitro-4-acetylaminophenol, giving an iminazole condensation product,



and by diazotisation and subsequent coupling with β -naphthol was converted into 4-hydroxy-3-carboxybenzenediazo- β -naphthol,

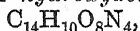


5-Nitro-3-aminosalicylic acid, obtained by reduction of the dinitrosalicylic acid, was converted through its *diazo-oxide* into 3-chloro-5-nitrosalicylic acid, 3-chloro-5-aminosalicylic acid, 3-bromo-5-nitrosalicylic acid, 3-bromo-5-aminosalicylic acid, and 5-nitro-3-cyanosalicylic acid. In addition to the preparation of various acetyl derivatives of these compounds there is described the production of the *benzyl* compound, $\text{C}_{14}\text{H}_{12}\text{O}_3\text{NCl}$, and of the *diazo-oxide*, $\text{C}_7\text{H}_3\text{O}_3\text{N}_2\text{Cl}$, derived from 3-chloro-5-aminosalicylic acid.

Experimental details will be found in the original. D. F. T.

Attempts to Prepare Asymmetric Quinquevalent Nitrogen Compounds. II. Nitrated Hydroxydiphenylamines.

RAPHAEL MELDOLA, HENRY STENNETT FOSTER, and RAINALD BRIGHTMAN (T., 1917, 111, 546—550. Compare preceding abstract).—2:4-Dinitro-4'-hydroxydiphenylamine was convertible into a monoacetyl and a diacetyl derivative, the former on nitration giving 2:4:?'-trinitro-4'-hydroxyacetyldiphenylamine,



whilst the latter was less readily nitrated and yielded 2:4:?:??:tetranitro-4'-hydroxyacetyldiphenylamine.

Other substances prepared were 2:4-dinitro-4'-hydroxydiphenylmethylamine, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, by the condensation of 4-chloro-1:3-dinitrobenzene with *p*-methylaminophenol; 2:4:6:3':5'-pentanitro-4'-hydroxydiphenylamine, $\text{C}_{12}\text{H}_6\text{O}_{11}\text{N}_6$, by the condensation of picryl chloride with isopicramic acid; and a substance, $\text{C}_{12}\text{H}_8\text{O}_7\text{N}_4$, by the action of nitric acid on 2:4:6-trinitro-4'-hydroxydiphenylamine in acetic acid.

Attempts to alkylate or benzylate these nitrated hydroxydiphenylamines gave discouraging results.

For experimental details see the original.

D. F. T.

Attempts to Prepare Asymmetric Quinquevalent Nitrogen Compounds. III. Hydroxyphenylglycine.

RAPHAEL MELDOLA, HENRY STENNETT FOSTER, and RAINALD BRIGHTMAN (T., 1917, 111, 551—553. Compare preceding abstracts).—A record of several fruitless attempts to prepare asymmetric quinone-ammonium compounds of the type $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}(\text{C}_7\text{H}_7) \cdot \text{C}_3\text{H}_5$ from hydroxyphenylglycine or its derivatives. In the course of the experiments *p*-nitrobenzylisopicramic acid, $\text{C}_{13}\text{H}_{10}\text{O}_7\text{N}_4$, was obtained from isopicramic acid and *p*-nitrobenzyl chloride.

For experimental details the original should be consulted.

D. F. T.

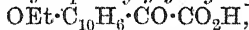
Preparation of a Bromo-derivative of *p*-Aminophenyl Salicylate. I. ABELIN, BERNE and S. LICHTENSTEIN-ROSENBLAT (D.R.-P., 297243, addition to D.R.-P., 291878; from *J. Soc. Chem. Ind.*, 1917, 36, 668. Compare A., 1916, i, 645).—*p*-Aminophenyl salicylate is treated with an α -bromodiethylacetyl haloid instead

of an α -bromoisovaleryl haloid, as in the original patent. The new product has a stronger sedative, anti-rheumatic, and soporific action, and is tasteless.
H. W.

Cyano-carbethoxy - 3 : 3 - dimethylcyclopentanone [Ethyl 2-Cyano-1 : 1-dimethylcyclopentane-3-one-2-carboxylate]. W. A. NOYES and C. S. MARVEL (*J. Amer. Chem. Soc.*, 1917, **39**, 1267—1271).—A further examination of the chemical properties of ethyl 2-cyano-1 : 1-dimethylcyclopentane-3-one-2-carboxylate (Noyes, A., 1899, i, 929). The *oxime* of this ester, m. p. 108—110° (Hewes, *Thesis*, Illinois, 1914), when heated with dilute sodium hydroxide solution is converted into 2-cyano-1 : 1-dimethylcyclopentan-3-oxime-2-carboxylic acid, $\text{OH}\cdot\text{N}:\text{C}_7\text{H}_{10}(\text{CN})\cdot\text{CO}_2\text{H}$, m. p. 142—143° (decomp.), which, when carefully heated, loses carbon dioxide with formation of 2-cyano-1 : 1-dimethylcyclopentan-3-oxime, $\text{OH}\cdot\text{N}:\text{C}_7\text{H}_{11}\cdot\text{CN}$, m. p. 127—128°. Hydrolysis of this substance or of its parent carboxylic acid with hydrochloric acid yielded carbon dioxide, ammonia, and presumably 1:1-dimethylcyclopentan-3-one (Blanc, A., 1908, i, 655), but the quantity was insufficient for definite identification.
D. F. T.

Syntheses in the Naphthalene Series. OLIVER KAMM, H. B. MCCLUGAGE, and A. W. LANDSTROM (*J. Amer. Chem. Soc.*, 1917, **39**, 1242—1248).—A search for a more convenient preparation and an independent proof of the structure of 1:4-ethoxynaphthoic acid (Gattermann, A., 1888, 575).

4-Ethoxy- α -naphthyl methyl ketone, prepared by the action of acetyl chloride on a carbon disulphide solution of α -ethoxynaphthalene in the presence of aluminium chloride, was oxidised with alkaline permanganate solution, with formation of α -ethoxynaphthoic acid, $[\alpha\text{-ethoxynaphthylglyoxylic}]$ acid,



m. p. 162°, and 1:4-ethoxynaphthoic acid, m. p. 217°. This acid was also obtained by oxidation of 1:4-ethoxynaphthaldehyde with alkaline permanganate. Reduction with sodium amalgam in hot alkaline solution converted the ethoxynaphthoic acid into 1:2:3:4-tetrahydro-1-naphthoic acid, the 2:3-dihydro-1-naphthoic acid and 1:2-dihydro-1-naphthoic acid being successive intermediate products. These results supply a complete demonstration of the structure of the 1:4-ethoxynaphthoic acid.
D. F. T.

Studies in Identification. IV. Identification of Alcohols. E. EMMET REID (*J. Amer. Chem. Soc.*, 1917, **39**, 1249—1255).—It has recently been shown that *p*-nitrobenzyl bromide reacts readily with the sodium salt of an acid to form an ester which, as a general rule, is crystalline (Reid, this vol., i, 333). By heating phthalic anhydride with an alcohol, the corresponding alkyl hydrogen phthalate is obtainable, primary alcohols reacting readily at 100°, whilst secondary alcohols need a temperature above 120°; the sodium salt derived from the acid ester is then convertible by the action of *p*-nitrobenzyl bromide into the corresponding alkyl

p-nitrobenzyl phthalate. The following mixed esters were obtained: *p*-nitrobenzyl methyl phthalate, m. p. 105·7°; *p*-nitrobenzyl ethyl phthalate, m. p. 80°; *p*-nitrobenzyl propyl phthalate, m. p. 53·0°; *p*-nitrobenzyl isopropyl phthalate, m. p. 74·0°; *p*-nitrobenzyl allyl phthalate, m. p. 61·5°; *p*-nitrobenzyl *n*-butyl phthalate, m. p. 62·0°; *p*-nitrobenzyl *n*-octyl phthalate, m. p. 41·0°; benzyl *p*-nitrobenzyl phthalate, m. p. 83·0°; *p*-nitrobenzyl phenylethyl phthalate, m. p. 84·3°; bornyl *p*-nitrobenzyl phthalate, m. p. 100°; isobornyl *p*-nitrobenzyl phthalate, m. p. 87°. The corresponding products derived from isobutyl, isoamyl, and cinnamyl alcohols, and from menthol and geraniol, were uncrystallisable oils.

D. F. T.

The Phenylsuccinic Acid Series. IV. *l*-Menthyl Esters of the Diphenylsuccinic Acids. H. WREN and CHARLES JAMES STILL (T., 1917, 111, 513—533; see also T., 1915, 107, 447, 1454).

—It has already been shown that aqueous-alcoholic potassium hydroxide converts ethyl *meso*diphenylsuccinate into a mixture of the potassium salts of *r*- and *meso*-diphenylsuccinic acids; the menthyl ester therefore promised to be of additional interest in view of the possibility that in its hydrolysis the dextro- and lævo-isomerides formed by the transformation of the *meso*-compound might not be produced in equimolecular proportion. The *l*-menthyl esters of diphenylsuccinic acid, however, proved too resistant to the action of alkali for the observation of this effect, even if it existed.

The diphenylsuccinic acids are not readily esterified by menthol. A mixture of *l*-diphenylsuccinic acid with excess of menthol at 115—120° in a current of hydrogen chloride yields a mixture of the *l*-menthyl hydrogen and di-*l*-menthyl esters. Under similar conditions, *d*-diphenylsuccinic acid gives *l*-menthyl hydrogen *d*-diphenylsuccinate as the only isolable product, and although a variety of methods was tried for the further conversion of this into the corresponding di-*l*-menthyl ester, the desired result was not attained. The racemic acid reacts with *l*-menthol under conditions similar to the preceding, giving rise to di-*l*-menthyl *l*-diphenylsuccinate, *l*-menthyl hydrogen *l*-diphenylsuccinate, *l*-menthyl hydrogen *r*-diphenylsuccinate, and *l*-menthyl hydrogen *d*-diphenylsuccinate. In this case the probable course of the change is the initial formation of *r*-diphenylsuccinic anhydride, which is subsequently converted into a mixture of the *l*-menthyl hydrogen esters of the *d*- and *l*-stereoisomeric acids; the *l*-menthyl hydrogen *l*-diphenylsuccinate, however, undergoes further esterification far more rapidly than the corresponding ester of the *d*-acid, so that the only isolable normal ester is that of the *l*-acid; the proportion of the acid esters of the *d*- and *l*-acids in the final mixture is disturbed by a partial resolution during the ethereal extraction, the potassium *l*-menthyl *d*-diphenylsuccinate being much more soluble than the corresponding *l*-diphenylsuccinate.

Di-*l*-menthyl *meso*diphenylsuccinate was prepared by heating the *meso*-acid with menthol at 150° in a current of hydrogen chloride, whilst the corresponding *r*-diphenylsuccinate was

obtained by the combination of equal quantities of the *d*- and *l*-diphenylsuccinates in acetone solution.

By the action of thionyl chloride on *l*-menthyl hydrogen *l*-diphenylsuccinate there was produced diphenylmaleic anhydride.

For experimental details reference must be made to the original. D. F. T.

Preparation of 1:5-Dihydroxynaphthalenedicarboxylic Acid. F. VON HEMMELMAYR (D.R.-P., 296501, addition to D.R.-P., 296035; from *J. Soc. Chem. Ind.*, 1917, **36**, 590).—Solid hydrogen carbonates are allowed to act on 1:5-dihydroxynaphthalene in presence of an indifferent solvent or medium, such as trichlorobenzene or nitrobenzene. H. W.

Lichens and their Characteristic Constituents. XV. O. HESSE (*J. pr. Chem.*, 1916, [ii], **94**, 227—270).—*Evernia furfuracea*, var. *olivetorina*. Continuing his investigation of the constituents of this lichen (A., 1911, i, 208), the author has now isolated, in addition to atranorin (about 0.25%) and olivetoric acid (about 2%), very small quantities of two new acids, which he names olivoric acid and *apoolivoric acid*.

Olivoric acid, $C_{23}H_{28}O_8$, faintly yellow, crystalline powder, m. p. 115—116°, which is insoluble in boiling light petroleum, forms an amorphous, easily soluble *potassium salt*, and in alcoholic solution develops a bluish-violet coloration with ferric chloride and a red coloration with calcium hypochlorite. *apoOlivoric acid*, $C_{23}H_{26}O_7$, leaflets, m. p. 108—109°, is soluble in boiling light petroleum, and in alcoholic solution gives a bluish-violet and a blood-red coloration with ferric chloride and with calcium hypochlorite respectively; in the case of both acids, the latter coloration disappears on further addition of the reagent.

By treatment with acetic anhydride and anhydrous sodium acetate, finally at 80—90°, olivetoric acid yields a *diacetyl derivative*, $C_{21}H_{24}O_7Ac_2$, a colourless varnish which is neutral to litmus, and is converted by hot water into a *monoacetyl derivative*, $C_{21}H_{25}O_7Ac$, colourless needles, m. p. about 116°, which in alcoholic solution is acid to litmus.

When heated with water at 150°, olivetoric acid yields carbon dioxide, olivetrollic acid, which has the composition $C_{19}H_{28}O_4$, not $C_{24}H_{34}O_5$ as recorded by Rave (*Diss.*, 1908), and *olivetorinol*, $C_{19}H_{24}O_6$, colourless leaflets, m. p. 104°. Olivetrollic acid forms colourless leaflets containing $2H_2O$, m. p. 26.5°, or anhydrous needles, m. p. 90°.

Parmelia saxatilis, var. *retiruga*.—This lichen has been shown to contain atranorin, saxatic acid, and an acid which was called protocetraric acid (A., 1903, i, 702); a small quantity of usnetic acid has also been isolated. The so-called protocetraric acid is not identical with the acid of this name obtained from *Cetraria islandica*, and has been renamed *parmatic acid* (Zopf's saxatilic acid).

Parmelia saxatilis, var. *omphalodes* (*Parmelia omphalodes*, L.).

—A specimen of this lichen gathered in the Carpathian Mountains was found to contain atranorin, usnetic acid, and parmatic acid, the last in considerable quantity. Another sample, collected at Hochkelch, Upper Alsace, yielded usnetic acid, parmatic acid (4.75%), atranorin, and a *substance*, $C_{24}H_{24}O_7$, needles, m. p. 197° , which is a lactone of usnetic acid, and appears to be identical with Knop's lobaric acid.

Pertusaria.—The constituents of this genus of lichens have been the subject of considerable dispute. The author is of opinion that the bitter variety grown on the beech contains, together with a little picrolichenin, salazinic acid as the only acid, whilst *Pertusaria* grown on the lime-tree contains no picrolichenin, but salazinic acid and a trace of a neutral, crystalline substance. Pure salazinic acid is tasteless, not bitter, as stated by Zopf. When heated with an excess of acetic anhydride at 90° for three hours, or at the b. p. for half an hour, salazinic acid yields *tetra-acetylsalazinic acid*, $C_{30}H_{20}O_{16}Ac_4$, colourless, crystalline meal, m. p. 211° , which is tasteless, and in alcoholic solution has an acid reaction, and does not give a coloration with a little ferric chloride. The elevation of the b. p. of an acetone solution of the acetyl derivative corresponds initially with this formula, but after long boiling the elevation is doubled. It seems, therefore, that *tetra-acetylsalazinic acid* is dimeric, the bimolecular β -form changing in solution into the monomeric α -form, $C_{15}H_{10}O_8Ac_2$ (compare Zopf, A., 1907, i, 218).

When salazinic acid is heated with anhydrous sodium acetate (1 part) and acetic anhydride (3 parts) at 90 – 100° for three hours, it yields α -*monoacetylsalazinic acid*, $C_{15}H_{11}O_8Ac$, colourless needles containing H_2O , m. p. about 120° (hydrated) or about 150° (anhydrous), which has a bitter taste, gives in alcoholic solution an acid reaction, and with a little ferric chloride a reddish-brown coloration, and is converted by warm aqueous sodium hydroxide into brick-red needles of the sodium salt of rubidic acid, $C_{11}H_{12}O_6$ (the author has formerly given to the acid the formula $C_{28}H_{24}O_{12}$, which would correspond with the bimolecular form).

Cetraria nivalis Ach.—This lichen contains *l*-usnic acid (1.8%) and a new acid, $C_{20}H_{26}O_6$, faintly brown powder, which is named *nivalic acid*. The latter develops a brownish-red coloration with ferric chloride in alcoholic solution.

After removal of the preceding constituents by ether, the remainder of the lichen yields to boiling water about 11% of carbohydrates, consisting as to about one-quarter of lichenin and as to about three-quarters of a new carbohydrate, which is named *l*-*Lichenidin*. The lichenin, $C_6H_{10}O_5$, is a colourless powder, m. p. about 275° (decomp., becoming brown at about 260°), which is optically inactive, does not give a coloration with iodine in aqueous solution, and yields only dextrose by hydrolysis with 5% sulphuric acid. *l*-*Lichenidin*, $C_{12}H_{22}O_{11}$, a colourless powder, does not give a coloration with iodine and has $[\alpha]_D^{15} -16.8^\circ$ in aqueous solution ($c=2$) in the presence of borax (1 mol.); it yields only dextrose by hydrolysis with boiling 5% sulphuric acid.

Cetraria islandica.—Zopf states (Flechtenstoffe, 1907) that

proto- α -lichesteric acid is identical with protolichesteric acid, despite a difference of 3.5 in the percentage of carbon. The author has examined samples of the lichen from different sources yearly since 1907, and has always found proto- α -lichesteric acid, except in two samples, which yielded an acid having the composition of protolichesteric acid, although, judging by some of its derivatives, it may be proto- α -lichesteric acid mixed with some unknown impurity.

Proto- α -lichesteric acid, $C_{18}H_{30}O_5$, forms leaflets, m. p. 107—108°. By slow heating a lower m. p. is observed, even as low as 92°, owing to a change into other acids, particularly dilichesteric and α -lichesteric acids; the same two acids are formed when a concentrated solution of proto- α -lichesteric acid in chloroform, acetone, alcohol, ether, or benzene is heated above 45°. Proto- α -lichesteric acid is converted into α -lichesteric acid by acetic anhydride at 90—100°, into lichestronic acid by boiling 10% potassium hydroxide, and into this acid and lichestrone by boiling aqueous barium hydroxide.

α -Lichesteric acid and dilichesteric acid do not occur as such in *C. islandica*, but are formed from the proto- α -lichesteric acid under the conditions stated above.

The author is of opinion that Zopf's protolichesteric acid is not an individual substance, but consists essentially of proto- α -lichesteric acid. Several times he has isolated acids, the composition and properties of which accorded well with those of protolichesteric acid ($C_{18}H_{30}O_4$), but since under the conditions stated above they yielded α -lichesteric, dilichesteric, and lichestronic acids, they are probably impure proto- α -lichesteric acid.

Cetrarinin has now been isolated from *Lichen island. concis.* as a colourless, crystalline powder, m. p. 228°; in alcoholic solution it does not change blue litmus or give a coloration with a little ferric chloride.

Contrary to statements in recent publications, cetraric acid does not occur as such in *C. islandica*, but is produced when attempts are made to obtain the bitter-tasting acids of the lichen through the agency of alcohol. If potassium carbonate and acetone instead of alcohol are employed, potassium fumarate and potassium protocetraric acid are obtained, whilst by the use of acetone alone fumarprotocetraric acid is extracted from the lichen.

The carbohydrates in *C. islandica*, which are soluble in boiling water, are stated in the literature to be lichenin and isolichenin. The latter is now found to consist of *d*-lichenidin and lichenoin. *d*-Lichenidin, $C_{12}H_{22}O_{11}$, is a white powder which has m. p. 270—280° (decomp.; darkening at about 240°), $[\alpha]_D^{15} + 15.4^\circ$ in water ($c=2$) in the presence of borax (1 mol.), does not give a coloration with iodine, and yields only dextrose by hydrolysis with boiling 5% sulphuric acid. Lichenoin, $C_{12}H_{20}O_{10} \cdot 4H_2O$, is an elastic substance like caoutchouc, which is easily soluble in cold water, and develops a blue coloration with iodine. After being dried in the air it becomes hard and inelastic. An aqueous solution of the substance dried at 100° has $[\alpha]_D^{18} + 202.7^\circ$ ($c=0.944$), does not give a precipitate with tannin and develops with iodine

a less intense blue coloration than does the air-dried material. The hydrolysis of lichenoin by 5% sulphuric acid is complete only after boiling for four hours, the products being dextrose and an optically inactive substance which is isolated as the compound, $2\text{C}_6\text{H}_{10}\text{O}_5 \cdot \text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, a colourless, hygroscopic powder having a neutral reaction in aqueous solution.

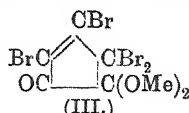
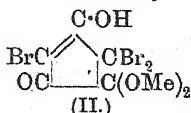
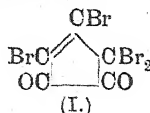
The carbohydrates in *C. islandica*, which are sparingly soluble or insoluble in hot water, yield after hydrolysis with sulphuric acid dextrose, a little *d*-galactose, and a trace of mannose.

C. S.

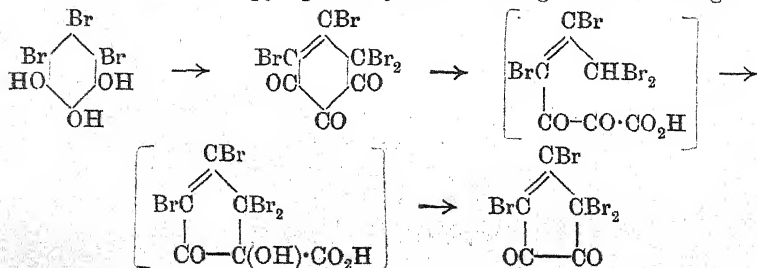
Diazotisation of 4-Bromo-4'-aminobenzophenone in Alcoholic Solution. P. J. MONTAGNE (*Chem. Weekblad*, 1917, 14, 526—529).—Diazotisation in alcoholic solution of 4-bromo-4'-aminobenzophenone produces a mixture of 4-bromobenzophenone, 4-bromo-4'-ethoxybenzophenone (m. p. 132°), and 4-bromo-4'-hydroxybenzophenone (m. p. 191°). The last compound can be separated from the mixture by means of alkali hydroxide, and the ethoxy-derivative partly by crystallisation from alcohol. The first compound is obtained free from the ethoxy-derivative by saponifying this with acetic acid and hydrobromic acid, and dissolving the hydroxy-compound formed by alkali hydroxide. The constitution of 4-bromo-4'-ethoxybenzophenone is established by its synthesis from 4-bromobenzoyl chloride, phenetole, aluminium chloride, and carbon disulphide.

A. J. W.

The Constitution of Xanthogallol. F. J. MOORE and RUTH M. THOMAS (*J. Amer. Chem. Soc.*, 1917, 39, 974—1011).—A careful study of xanthogallol and its derivatives has led to the conclusion that the constitution assigned to this compound by Theurer (compare A., 1888, 1084) is incorrect, since it is not in accord with present molecular weight determinations or analyses, as the compound is now shown to contain no hydrogen. A much simpler cyclic formula (I) is suggested, based mainly on several series of reactions

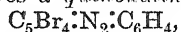


leading to oxalic acid and brominated acetones. This formula also permits a simple interpretation of the reaction by which xanthogallol is formed from pyrogallol by the following series of changes:



Molecular weight determinations by the cryoscopic method give values ranging from 379—403, whereas the formula put forward by Stenhouse (compare this Journal, 1874, 586) and confirmed by Theurer requires 1436. For the hydrogen determinations, combustions were performed using 1 gram samples, to eliminate error due to moisture, and no hydrogen was found to be present. The new formula gives a good account for the composition and relationships of all of Theurer's derivatives and also of certain new ones. These are set out in detail in the original.

No less than three independent methods of decomposition of xanthogallol lead to oxalic acid or its derivatives, thus confirming the adjacent position of the carbonyl groups. Further, with *o*-phenylenediamine it gives a *quinoxaline* derivative,

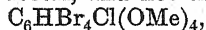


m. p. 186—187°, free from oxygen. The aniline derivative of xanthogallol (*loc. cit.*) also gives a *quinoxaline* derivative,

$\text{NHPh} \cdot \text{C}_5\text{Br}_3 \llcorner \text{N} \gg \text{C}_6\text{H}_4$, decomposing at 210°, and a similar com-

-pound, $\text{C}_5\text{Br}_3\text{Cl} \llcorner \text{N} \gg \text{C}_6\text{H}_4$, m. p. 171—172°, is obtained from chloroxanthogallol.

When hydrogen chloride is passed into a solution of xanthogallol in methyl alcohol, the product is not chloroxanthogallol methyl acetal, but xanthogallol methyl acetal (formula III) with a certain amount of the chlorinated acetal. The latter acetal with alkali gives the methyl acetal of hydroxyxanthogallol (formula II), which with hydrochloric acid in methyl alcohol gives the *methyl ether* of this acetal, and not the compound,



as stated by Theurer. The position of the hydroxyl group in hydroxyxanthogallol, and that of the reactive bromine atom in xanthogallol, is confirmed by the fact that hydroxyxanthogallol is decomposed by bromine water, giving oxalic acid and pentabromoacetone. The behaviour of hydroxyxanthogallol towards aniline and *p*-toluidine is different from that given by Theurer. If *p*-toluidine is added in insufficient amount to the hydroxy-compound in alcohol, a compound, m. p. 89—90°, is obtained, which is the *p*-toluidine salt. When this is crystallised from alcohol or dilute acetic acid, a hydrated product, m. p. 102—104°, is obtained which when dried gives a compound, m. p. 147—148°. In the formation of these last two compounds the toluidine molecule must have migrated to one of the carbonyl groups, since with aniline they both give oxanilide-*p*-toluidide. Similarly with aniline, the *aniline* salt, m. p. 70°, is obtained, which is converted into a compound, m. p. 148—149°, which with aniline gives oxanilide, and with *p*-toluidine, oxanilide-*p*-toluidide.

The acid, m. p. 124° mentioned by Theurer as obtained from xanthogallol by the action of sodium hydroxide is best prepared from hydroxyxanthogallol and alkali, and is now named *xanthotonic acid*, m. p. 110—115°, and assigned the constitution $\text{CHBr} \cdot \text{C}(\text{OH}) \cdot \text{CBr}_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$. With bromine water in the cold it

gives pentabromoacetone, and with hydrochloric acid and potassium chlorate *chlorotribromoacetone*,

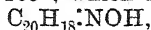


m. p. 64—65°.

W. G.

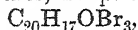
Action of γ -Diketones on Unsaturated Ketones. M. SCHOLTZ (*Arch. Pharm.*, 1916, 254, 547—566, 625).—The reaction between acetylacetone and phenyl cinnamylidenemethyl ketone has been examined in the expectation that the conjugation of the double linkings of the latter would determine the course of the reaction. This expectation has not been confirmed.

When an alcoholic solution of phenyl cinnamylidenemethyl ketone (1 mol.) and acetylacetone (2 mols.) is boiled for three hours with 20% aqueous sodium hydroxide (2 mols.), two substances, $\text{C}_{20}\text{H}_{18}\text{O}$ and $\text{C}_{22}\text{H}_{24}\text{O}_4$, are produced in about equal quantities. The former, which alone is produced when the reaction is effected in absolute alcohol and sodium ethoxide is used instead of sodium hydroxide, is a neutral substance crystallising in colourless plates, m. p. 105°, which forms an *oxime*,



needles, m. p. 173°; *semicarbazone*, needles, m. p. 187°;

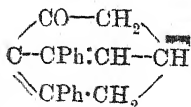
dibromide, $\text{C}_{20}\text{H}_{18}\text{OBr}_2$, needles, m. p. 167°; *tribromide*,



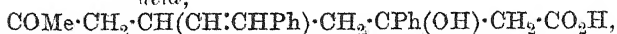
rhombic plates, m. p. 204° (by loss of hydrogen bromide from the initially formed tetrabromide); and *tetrachloride*, needles, m. p. 72—74°. From the researches of Michael (1887), Auwers (1891), and Knoevenagel (1894—1903) on this type of reaction, there can be no doubt that the substance $\text{C}_{20}\text{H}_{18}\text{O}$ is 1-phenyl-5-styryl- Δ^1 -

cyclohexen-3-one, $\text{CHPh}:\text{CH}:\text{CH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CPh} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} \text{CH}$, produced by the successive operations of addition of the two reacting substances, ring closure with the elimination of water, and hydrolysis of the acetyl group in position 4.

Only one of the two possible dibromides is produced by the addition of bromine (1 mol.), and its constitution has not been determined. When its alcoholic solution is heated with 50% aqueous potassium hydroxide on the water-bath, two molecules of hydrogen bromide are eliminated, and a substance, $\text{C}_{20}\text{H}_{16}\text{O}$, pointed prisms, m. p. 181°, is produced, which is regarded as 1-phenyl-2:5-endophenylvinylene- Δ^1 -cyclohexen-3-one (annexed formula).

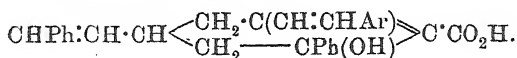


The second substance, $\text{C}_{22}\text{H}_{24}\text{O}_4$, mentioned above, is β -hydroxy- ζ -keto- β -phenyl- δ -styryloctoic acid,



produced by the addition of 1 mol. of each of the two reacting substances and of 1 mol. of water. It crystallises in colourless needles, m. p. 120°, forms stable salts (*sodium salt*, $\text{C}_{22}\text{H}_{23}\text{O}_4\text{Na}$, needles), and yields a *semicarbazone*, rhombic plates, m. p. 171°, and *phenylhydrazone*, faintly yellow needles, m. p. 134°. Its unsaturated nature is shown by the addition of bromine and by the

instant decolorisation of potassium permanganate by its solution in aqueous sodium carbonate. Under the influence of dilute sodium hydroxide solution, it condenses readily with aromatic aldehydes; the products, however, are not the expected arylidene derivatives produced by condensation at the terminal methyl group, but substances of this composition minus the elements of one molecule of water. The author is of opinion that ring closure, as well as condensation, has occurred, and that the products are *cyclohexene-carboxylic acids* having the constitution

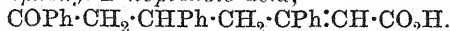


Benzaldehyde, furfuraldehyde, *p*-tolualdehyde, anisaldehyde, cinnamaldehyde, and *m*-nitrobenzaldehyde all condense in this way and the products are: Ar=Ph, colourless needles, m. p. 193°; Ar=C₄H₉O, faintly yellow prisms, m. p. 184°; Ar=*p*-C₇H₇, colourless prisms, m. p. 194°; Ar=*p*-OMe·C₆H₄, prisms, m. p. 187°; Ar=CHPh:CH, colourless needles, m. p. 191°; and Ar=*m*-NO₂·C₆H₄, yellow needles, m. p. 204°.

Under the conditions given above the reaction between *p*-tolyl cinnamylidenemethyl ketone and acetylacetone is quite similar to that between phenyl cinnamylidenemethyl ketone and acetylacetone. The two products are 1-*p*-tolyl-5-styryl-Δ¹-cyclohexen-3-one, C₂₁H₂₀O, colourless leaflets, m. p. 109° (*semicarbazone*, needles, m. p. 115°), and β-hydroxy-ζ-keto-β-*p*-tolyl-δ-styryloctioic acid, C₂₃H₂₆O₄, colourless needles, m. p. 106°.

When phenyl cinnamylidenemethyl ketone reacts with benzoylacetone under the conditions given above, only one substance (apart from a considerable quantity of benzoic acid) is produced. This, which is obtained only in small yield, is an acid, C₂₇H₂₆O₄, colourless rods, decomp. 185—186°, beginning at about 160°, and is regarded as β-hydroxy-ζ-keto-βζ-diphenyl-δ-styrylheptoic acid, C₂₇H₂₆O₄, colourless needles, m. p. 167°.

The reaction between phenyl styryl ketone and benzoylacetone under the conditions given above yields Knoevenagel's 1:5-diphenyl-Δ¹-cyclohexen-3-one and an acid, C₂₅H₂₂O₃, colourless rods, m. p. 202° (decomp. beginning at about 180°), which is regarded as ζ-keto-βδζ-triphenyl-Δ^α-heptenoic acid,



Phenyl styryl ketone and acetylacetone react to form 1:5-diphenyl-Δ¹-cyclohexen-3-one and ζ-keto-βδ-diphenyl-Δ^α-octenoic acid, which could not be obtained crystalline but forms a *semicarbazone*, C₂₁H₂₂O₃N₃, needles, m. p. 170°.

C. S.

Preparation of 2-Aminoanthraquinone and its Derivatives.

FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 295624; from *J. Soc. Chem. Ind.*, 1917, **36**, 542).—2-Aminoanthraquinone and its

derivatives are prepared by heating 2-chloroanthraquinone, or such of its derivatives as do not contain a strongly negative substituent (carboxyl, halogen, nitro-, or sulphonic group) in the ortho-position to the chlorine atom, with aqueous ammonia under pressure, either with or without copper or copper salts. H. W.

Preparation of Benzoyl Derivatives of β -Hydroxy- or $\alpha\beta$ -Di- and Poly-hydroxyanthraquinones. R. WEDEKIND & Co. (D.R.-P., 297261; from *J. Soc. Chem. Ind.*, 1917, **36**, 638—639).—The process applies particularly to 2-hydroxyanthraquinone, 2:6- and 1:2-dihydroxyanthraquinone, and 1:2:6- and 1:2:7-trihydroxyanthraquinone, which are treated with benzoic acid with or without the addition of sulphuric acid. The weight of benzoic acid taken is ten to fifteen times that of the hydroxyanthraquinone, and although the sulphuric acid accelerates the reaction, it is not essential. Action is completed by heating the mixture at atmospheric pressure. The process obviates the employment of benzoyl chloride. H. W.

Commercial Chrysarobin. II. ROBERT EDER (*Arch. Pharm.*, 1916, **254**, 1—33. Compare A., 1915, i, 823).—The oxidation products of chrysarobin having been described (*loc. cit.*), the examination of chrysarobin itself has now been undertaken. In order to stabilise its reactive constituents, the chrysarobin (obtained from the same consignment as that used in the oxidation experiments, *loc. cit.*) is first acetylated or benzoylated.

Chrysarobin is boiled for one hour with acetic anhydride and sodium acetate, the solution is poured on ice, and the dark oil is converted by agitation with water into a crude acetate, a brown, friable powder. This is separated by boiling glacial acetic acid into a crystalline orange-yellow powder (A), m. p. 230°, and an amorphous substance (B), which remains in solution in the acetic acid. The substance A agrees in its properties and m. p. with Liebermann's "acetylchrysarobin" (Liebermann's "chrysarobin" and its acetyl derivative [1878—1888] are shown to be, not individual substances, but mixtures of two different anthranols); it, however, contains methoxyl, and is found to be a mixture of triacetylemodinanthranol monomethyl ether (about one-third) and triacetylchrysophanic acid anthranol (about two-thirds). The two constituents cannot be separated by means of solvents, even after hydrolysis, but after demethylation a separation of the products can be effected. The demethylation cannot be brought about by concentrated sulphuric acid, and only imperfectly by a mixture of glacial acetic and concentrated hydrochloric acids at 190°; a boiling mixture of hydriodic acid, D 1.70, and acetic anhydride in equal volumes gives a satisfactory result in the absence of air, and the demethylated product is separated by boiling chloroform into emodinanthranol (yielding emodin by oxidation with chromic acid) and chrysophanic acid anthranol (yielding chrysophanic acid by oxidation).

The composition of the substance *A* has also been ascertained by comparing it with mixtures of triacetylchrysophanic acid anthranol and triacetylemodinanthranol monomethyl ether, separately prepared. These two substances are extraordinarily similar to one another in almost every respect. Their crystals cannot be differentiated under the microscope, they have about the same solubility in the usual solvents, their m. p.'s are almost identical and are lowered by only a few degrees in mixtures of the two substances.

The amorphous substance *B*, which represents about 75% of the product obtained by acetylating chrysarobin, contains a small amount of diacetylemodin monomethyl ether. The main portion, however, is a pale yellow, amorphous powder which, after successive oxidation with chromic and acetic acids at 60° and hydrolysis with boiling 5% alcoholic hydrochloric acid, can be separated by evaporation with a little 10% sodium carbonate solution and extraction of the dried residue with benzene into chrysophanic acid (impure) and emodin.

The m. p. of specially purified diacetylchrysophanic acid is found to be 208°.

An attempt is made to ascertain in what form the chrysophanic acid obtained from the amorphous acetates *B* exists in the original chrysarobin. According to Tutin and Clewer's view, chrysarobin contains, in addition to much chrysophanic acid anthranol, about 5% of chrysophanic acid. The author has been unable to isolate diacetylchrysophanic acid from the amorphous acetates *B*, but by reducing chrysarobin in boiling glacial acetic acid with tin and hydrochloric acid and acetylating the reduced product, he has shown that the amount of triacetylchrysophanic acid anthranol formed is greater than that obtained by acetylating unreduced chrysarobin. This result supports Tutin and Clewer's view, but the author suggests an alternative explanation of the increase.

Chrysarobin has been benzoylated in two different ways, which lead to different results. When treated by the Schotten-Baumann method in an atmosphere of hydrogen, chrysarobin yields dibenzoylemodin monomethyl ether (m. p. 233—234°, not 228°, as stated, *loc. cit.*) and dibenzoyldehydroemodinanthranol monomethyl ether, m. p. 235—255° (decomp.), in small quantity, together with considerable amounts of amorphous, unidentified products. In the second method of benzoylation, chrysarobin was boiled with benzoyl chloride until hydrogen chloride ceased to be evolved. After basifying with 20% sodium hydroxide, the product was found to consist mainly of resinous substances, but dibenzoylemodin monomethyl ether and *tribenzoylemodinanthranol monomethyl ether*, $C_{36}H_{28}O_6(OMe)$, yellow prisms, m. p. 265—266°, were isolated. In view of the results obtained by the acetylation of chrysarobin, it is remarkable that tribenzoylchrysophanic acid anthranol is not produced by benzoylation. It has been prepared by heating a pyridine solution of chrysophanic acid anthranol with benzoyl chloride on the water-bath. *Tribenzoylchrysophanic acid anthranol*, $C_{36}H_{24}O_6$, yellow prisms, m. p. 260°, resembles tri-

benzoylmodinanthranol monomethyl ether as closely as the corresponding triacetyl derivatives resemble one another.

As the results of these experiments and of those previously recorded (*loc. cit.*), the following constituents of chrysarobin have been definitely identified: chrysophanic acid anthranol, emodin-anthranol monomethyl ether, emodin monomethyl ether, dehydro-emodinanthranol monomethyl ether, and emodin (or emodin-anthranol). The author has been unable to detect in his sample of chrysarobin Jowett and Potter's dichrysarobin methyl ether, dichrysarobin, and the substance $C_{17}H_{14}O_4$, Hesse's chrysarobol and chrysophanic acid anthranol methyl ether, and Tutin and Clewer's chrysophanic acid and ararobinol; in other respects his results show an extensive agreement with those of the last-mentioned authors, which were attained by quite different methods. C. S.

Complete Synthesis of a Fenchene. GUST. KOMPPA and R. H. ROSCHIER (*Ann. Acad. Sci. Fennica*, 1916, [A], 10, iii, 3—15; from *Chem. Zentr.*, 1917, i, 751—752).— α -Fenchene has been prepared from α -fenchocamphorone, thereby completing the synthesis of the former.

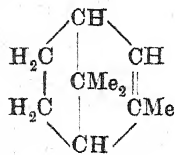
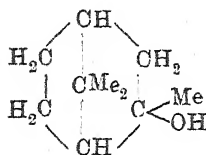
α -Fenchocamphorone, b. p. 196—197° (semicarbazone, m. p. 220°), is converted by magnesium methyl iodide into the alcohol (annexed formula), b. p. 86·5—87°/14 mm., which, when distilled under atmospheric pressure, loses water and yields α -fenchene, b. p. 154—156°, D_4^{20} 0·8660, D_D^{20} 1·47045, M.R. 43·93. The latter is transformed by ozone into r - α -fenchocamphorone (semicarbazone, m. p. 220°) and a monobasic acid, m. p. 105°, which is identical with r - α -fenchenylic acid.

*cyclo*Fenchene hydrochloride, obtained by the action of hydrogen chloride on fenchene, has m. p. 26—29° (Aschan gives m. p. 27·5—29°), and is converted by aniline into isopinene, $C_{10}H_{16}$, b. p. 154—155°, D_4^{20} 0·8671, n_D^{20} 1·47153, M.R. 43·91. It yields a hydrochloride, m. p. 35—37°. When ozonised in acetic acid solution, isopinene yields α -fenchocamphorone (semicarbazone, m. p. 219—220) and r - α -fenchenylic acid, m. p. 104—105°, identical with the products obtained from α -fenchene. The synthetic hydrocarbon and isopinene are therefore identical and constitute r - α -fenchene (annexed formula). *iso*Pinene is

oxidised by alkaline permanganate to r -hydroxy- α -fenchenic acid, m. p. 139—140°. The fenchenic acid obtained by Aschan from isopinene (*Öfversigt Finska Vetensk. Soc. Förh.*, 1908—9, [A], 51, No. 9, 10) is probably apocamphoric acid contaminated with *dl*-hydroxy- α -fenchenic acid.

Wallach's r - α -fenchene (A., 1908, i, 811) on ozonisation yields α -fenchocamphorone and r - α -fenchenylic acid, m. p. 105°.

Sodium hypobromite solution transforms r -hydroxy- α -fenchenic acid, m. p. 140°, into fenchocamphorone, which is further con-



verted into a product, m. p. 50—54° (probably a bromofenchocamphorone), and an *acid*, m. p. 147—148°, which contains bromine. *apo*Camphoric acid could not be identified. The observation of Aschan (*loc. cit.*) that bromoform is eliminated during this action is probably erroneous, since the odour of fenchocamphorone and hypobromite solution resembles that of bromoform.

r- α -Fenchene hydrochloride, obtained from Wallach's α -fenchene and hydrogen chloride, has m. p. 55—37°, b. p. 81°/12 mm., and then m. p. 33—35°; it does not depress the m. p. of the hydrochloride prepared from *isopinene*. H. W.

The Oleoresin of Douglas Fir. A. W. SCHORGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1040—1044. Compare Rabak, *Pharm. Rev.*, 1904, **22**, 293).—Samples of oleoresin were obtained from the heartwood and living wood of the Douglas fir. The oleoresin from the heartwood contained a volatile oil consisting chiefly of highly rotatory *l*- α -pinene with small amounts of *l*-limonene and *l*-terpineol. That from the sapwood contained an oil consisting of *l*- α -pinene, *l*- β -pinene, and probably a little *l*-limonene. The so-called firpene described by Frankforter and Frary (compare A., 1906, i, 970, 971) as occurring in this oleoresin is probably highly active *l*- α -pinene, the activity accounting for the fact that no nitroschloride was obtained from it (compare Tilden, T., 1904, **85**, 759). W. G.

Further Syntheses of Glucosides by Means of Acetobromoglucose and Quinoline. Derivatives of Menthol and Resorcinol. EMIL FISCHER and MAX BERGMANN (*Ber.*, 1917, **50**, 711—722. Compare this vol., i, 216).—The α - and β -glucosides of menthol and their acetates, and the penta-acetate of the β -glucoside of resorcinol, have been prepared, starting with acetobromoglucose, quinoline, and menthol or resorcinol. α -Menthylglucoside can be obtained more easily than any other synthetic glucoside of a cyclic compound known as yet, and will undoubtedly be of interest for physiological studies.

Acetobromoglucose (50 grams), *l*-menthol (110), and quinoline (20) are heated at 100—105°, the base is extracted with dilute sulphuric acid and ether, the washed ethereal solution is evaporated, and the water and excess of menthol removed by heating at 100°/0.2 mm. The product is a mixture of the tetra-acetates and lower acetates of the α - and β -glucosides. For the purpose of isolating the tetra-acetates, the mixture is acetylated by means of acetic anhydride and pyridine in the cold, and then the glucosides are separated by crystallisation from dilute alcohol. Tetra-acetyl- β -menthylglucoside separates first, in long, flat, glistening needles, m. p. 131—132° (corr.), $[\alpha]_D^{17}$ -66.0° in benzene, and β -menthylglucoside can be readily obtained from this by means of aqueous-alcoholic barium hydroxide at 60°, in large plates, 1H₂O, m. p. 75—76°, which lose water at 56°/15 mm., and then have $[\alpha]_D^{20}$ -93.7°, in alcohol (compare A., 1909, i, 365). The more

soluble *tetra-acetyl- α -menthylglucoside* crystallises in stellate aggregates of prisms, m. p. 82—83°, $[\alpha]_D^{20} + 94.4^\circ$, in benzene.

Triacetates can be isolated by fractional crystallisation from the original crude product. *Triacetyl- β -menthylglucoside* separates in radiating needles, m. p. 143° (corr.), $[\alpha]_D^{18} - 12.73^\circ$, and *triacetyl- α -menthylglucoside* in large, flat prisms, m. p. 99—100°, $[\alpha]_D^{20} + 107.5^\circ$.

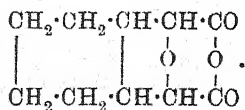
α -*Menthylglucoside*, $C_{16}H_{30}O_6 \cdot H_2O$, is very sparingly soluble in cold water, and crystallises quickly from 2000 parts of hot water on cooling. For this reason it is very easily isolated, and so the crude mixture obtained at the outset, or the triacetates, or the still lower acetates left in the mother liquors may be worked up for this glucoside. Starting with acetobromoglucose, the yield of α -menthylglucoside may be as much as 50%. It crystallises from acetone in prisms, m. p. 159—160° (corr.), $[\alpha]_D^{20} + 64.2^\circ$ in alcohol.

The hydrolysis of α - and β -menthylglucosides was tested in the usual way. The β -glucoside is somewhat more rapidly hydrolysed by acids than the isomeride, and yeast extract and emulsin also behave normally.

With resorcinol, the mixture of acetyl derivatives obtained by the above method is so complex that it is best to acetylate it completely to *penta-acetyl- β -resorcinolglucoside* (*tetra-acetyl- β -in-acetoxyphenylglucoside*) by means of acetic anhydride and pyridine. This crystallises in long, radiating needles or prisms, m. p. 118—119° (corr.), $[\alpha]_D^{18} - 40.1^\circ$, in benzene. The known β -resorcinolglucoside (A., 1912, i, 884) is then conveniently obtained by hydrolysis with barium hydroxide. J. C. W.

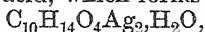
Digitalis Glucosides. H. KILIANI (*Arch. Pharm.*, 1916, 254, 255—295).—An account of work already published (A., 1915, i, 281; 1916, i, 493; also A., 1914, i, 309, 857). C. S.

Cantharidin. V. WALTER RUDOLPH (*Arch. Pharm.*, 1916, 254, 423—456).—In some cases one, in other cases another, of the three formulæ for cantharidin proposed by Gadamer (*Arch. Pharm.*, 1914, 252, 609) serves to explain the reactions described by the author in this and in his preceding paper (*ibid.*, 636). Before a preference in favour of any one of the three formulæ can be expressed, the constitutions of cantharene and of the acid obtained by the pyrogenic decomposition of barium cantharate must be determined. The author attacks the former problem, leaving the latter to Gadamer. He also examines the substance $C_{10}H_{14}O_3$, which he calls *cantharidide*, obtained by Anderlini in 1893 by reducing cantharidin by sodium and ethyl alcohol. This proves to be a neutral substance exhibiting the properties of a very stable lactone, and is not identical with the product obtained by the reduction of the "dibromide" of cantharidin. In the author's opinion, these facts serve to eliminate the second of Gadamer's three formulæ (annexed).



The acid anhydride group of cantharidin is so stable that the corresponding acid, cantharidic acid, cannot be isolated and is

only known in aqueous solution. When the "dibromide" is reduced by zinc and zinc dust in acetic and dilute sulphuric acids, the product possesses this property to a very much less pronounced degree, and the acid itself, *deoxycantharidic acid*, $C_{10}H_{16}O_4$, crystals, m. p. 160—165° to a turbid liquid, can be isolated, although it is still contaminated with 10—15% of the anhydride, *deoxycantharidin*. The acid, which forms a silver salt,



cannot be converted, curiously enough, into its anhydride by heating in a vacuum at 70°; the change is effected, however, by fusion or by boiling with water. Deoxycantharidin is a colourless, friable substance which is slowly volatile with steam and has an odour recalling that of camphor. Attempts to resolve deoxycantharidic acid into optically active components by means of the brucine salt were unsuccessful.

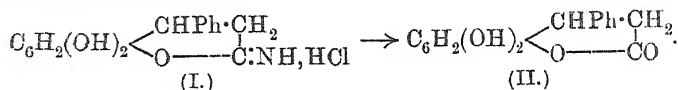
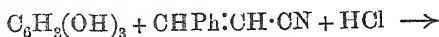
The "dibromide" of cantharidin is converted by methylalcoholic hydrogen bromide, even after keeping for a week, only into a *methyl hydrogen ester*, $C_{11}H_{16}O_4Br_2$, m. p. 122°, becoming turbid at 120°; when the preparation is conducted with methylalcoholic hydrogen chloride on the water-bath, a liquid substance ($C_{11}H_{16}O_4Br_2$), b. p. 132—133°/14 mm., is obtained, which appears to be the methyl hydrogen ester deprived of the elements of 1 molecule of hydrogen bromide. The failure of the "dibromide" of cantharidin to yield a dimethyl ester is attributed to steric hindrance, and on this account the preference is given to the formula (annexed) of Gadamer's remaining two formulae of cantharidin. This preference is supported by the fact that cantharene, prepared by boiling the "dibromide" of cantharidin with 25% aqueous potassium hydroxide in an atmosphere of hydrogen, has a smaller exaltation of the molecular refraction than the values previously recorded (compare Haworth, T., 1913, 103, 1242). The author has not succeeded in obtaining *o*-toluic acid by the oxidation of cantharene under Piccard's conditions.

C. S.

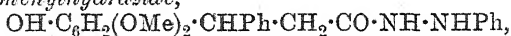
Formation of Hydrocoumarin Derivatives (Dihydro- α -benzopyrones) from Phloroglucinol. EMIL FISCHER and OSMAN NOURI (*Ber.*, 1917, 50, 693—701).—Whereas ordinary nitriles give rise to ketones when condensed with phloroglucinol by Hoesch's method (A., 1915, i, 820; this vol., i, 342), unsaturated nitriles yield derivatives of dihydrocoumarin. Unstable imines are formed as intermediate products, as in the production of γ -benzopyrones by the condensation of acylacetone nitriles with pyrogallol (Ghosh, A., 1916, i, 281), but these are readily hydrolysed by water to the α -benzopyrone derivatives.

Cinnamonnitrile and phloroglucinol are dissolved in ether, mixed with powdered zinc chloride, and the chilled solution saturated with hydrogen chloride. The granular hydrochloride of the intermediate imine (I.) gradually separates and this yields 5:7-dihydroxy-4-phenyl-3:4-dihydro-1:2-benzopyrone (II.) on heating with

water. The compound crystallises in slender needles, m. p. 211° (corr.) and forms a *diacetate*, m. p. 147—148° (corr.).



The same substance can be obtained by the reduction of the corresponding 5:7-dihydroxy-4-phenyl-1:2-benzopyrone ("m-di-hydroxy- β -phenylcoumarin"; Kostanecki and Weber, A., 1894, i, 88). When treated with diazomethane, it gives rise to the 5:7-di-methoxy-derivative, which crystallises in long needles or stout prisms, m. p. 131—132° (corr.). This may be converted into β -phenyl- β -2:4:6-trimethoxyphenylpropionic acid, large columns or tablets, m. p. 156—157° (corr.), by first opening the ring by hydrolysis with aqueous-alcoholic sodium hydroxide, methylating the free acid obtained, by adding the ethereal extract to cold ethereal diazomethane, and finally hydrolysing the methyl ester. The 5:7-dimethoxy-compound may also be transformed into β -phenyl- β -2-hydroxy-4:6-dimethoxyphenylpropionamide, m. p. 185—186° (decomp.), by the action of methyl-alcoholic ammonia at 50—60° in a sealed tube, or into β -phenyl- β -2-hydroxy-4:6-dimethoxyphenylpropion- ω -phenylhydrazide,



long prisms, m. p. 171—172° (corr.), by warming with phenylhydrazine.

p-Coumaronitrile condenses with phloroglucinol under the above conditions to form 5:7-dihydroxy-4-*p*-hydroxyphenyl-3:4-dihydro-1:2-benzopyrone, which crystallises in slender needles, m. p. indefinite, about 270°.

Ethyl phenylpropiolate condenses with phloroglucinol to give a high yield of the above-mentioned 5:7-dihydroxy-4-phenyl-1:2-benzopyrone, m. p. 238—239° (corr.).

J. C. W.

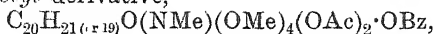
Alkaloidal Derivatives of Mercuric Nitrite. PRAFULLA CHANDRA RAY (T., 1917, 111, 507—510. Compare T., 1912, 101, 616).—Compounds of mercuric nitrite with aliphatic and aromatic amines and with heterocyclic bases have already been obtained (*loc. cit.*), and the author now describes compounds with various alkaloids, viz., nicotine, coniine, quinine, quinidine, cinchonidine, codeine, narcotine, strychnine, brucine, and cocaine. Experiments on the electrical conductivity of aqueous solutions of the cinchonidine and cocaine compounds, which contain the alkaloid and mercuric nitrite in molecular proportion, indicate the formation of three ions in each case.

For experimental details see the original.

D. F. T.

Aconite Alkaloids. Pyraconitine and Pyraconine. HEINRICH SCHULZE and A. LIEBNER (*Arch. Pharm.*, 1916, 254, 567—583).—Pyraconitine, obtained by heating aconitine or japaconitine at 192°

(A., 1913, i, 1375), does not interact with ketone reagents, but forms a *diacetyl* derivative,



stout crystals containing 1EtOH from alcohol, m. p. 213° , softening at about 202° (dried, m. p. 208°), which forms an *aurichloride*, yellow crystals, decomp. 214° ; *hydriodide*, stout needles, m. p. $260\cdot5^\circ$; and *perchlorate*, crystals, m. p. $282\text{--}283^\circ$ (decomp.).

The remaining uncharacterised oxygen atom in pyraconitine is present probably in the ethylene oxide form, since it is unaffected by ketone reagents, by acylating reagents, and by water at 192° ; by heating pyraconitine with methyl alcohol at 130° methyl benzoate and pyraconine are formed, whilst methyl iodide at 100° has no action.

Since Dunstan and Carr's pyraconitine (T., 1894, **65**, 176) is identical with Dunstan and Read's pyrojapaconitine (T., 1900, **77**, 60), it follows that the pyraconine prepared from the former must be identical with the pyrojapaconine prepared from the latter. This is shown to be the case. Pyraconine has not been obtained crystalline, but it forms well-crystallised salts; the hydrochloride forms large crystals containing $2\frac{1}{2}\text{H}_2\text{O}$, m. p. $134\text{--}135^\circ$ (decomp.), $[\alpha]_D -124\cdot6^\circ$ in aqueous solution (Dunstan and Carr give m. p. 154° and $[\alpha]_D -102\cdot07^\circ$); the *hydrobromide* forms stout crystals containing $2\text{H}_2\text{O}$, decomp. 143° (anhydrous, $146\text{--}147^\circ$); the *hydriodide* forms crystals containing $1\text{H}_2\text{O}$, m. p. $224\cdot5^\circ$ (decomp.); and the *perchlorate* forms anhydrous crystals, darkening at 235° , m. p. 243° , decomp. 244° .

Four of the oxygen atoms in pyraconine are present in methoxy groups. Three of the remaining four are present in hydroxyl groups, since *triacetylpyraconine*, $\text{C}_{31}\text{H}_{45}$ (or 43) O_{11}N , stout colourless prisms, m. p. 231° , has been prepared.

Pyraconitine does not undergo reduction when it is treated by the Paal-Skita method. Its hydrobromide appears to exist in two different forms, which are only distinguishable by their m. p.'s, 150° (decomp.) (anhydrous, 177°) and 240° (decomp. at 242°) (anhydrous, $243\text{--}244^\circ$ [decomp.]) respectively, the m. p. of the mixture being about 150° .

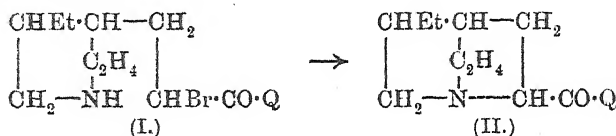
C. S.

The Cinchona Alkaloids. ADOLF KAUFMANN (*Ber.*, 1917, **50**, 701—702).—A claim for priority over Rabe (compare this vol., i, 216). J. C. W.

The Influence of Varying Concentration of Hydrogen Ion on the Optical Rotation of the Isomeric Alkaloids, Cinchonine, Cinchonidine and Cinchotoxine. H. C. BIDDLE and THOMAS WATSON (*J. Amer. Chem. Soc.*, 1917, **39**, 968—974. Compare A., 1915, ii, 759).—The specific rotation in the case of these three alkaloids is a direct function of the concentration of the bivalent alkaloid ion and is independent of the inactive acid ion. The univalent cinchonine ion has $[\alpha]_D^{15} = +205\cdot6^\circ$ and the bivalent ion $[\alpha]_D^{15} = +253\cdot1^\circ$. The corresponding values for the cinchonidine ions are $[\alpha]_D^{15} = -141\cdot1^\circ$ and $-185\cdot6^\circ$ respectively. The value of

the second dissociation constant of cinchonine at 16° was found to be 2.05×10^{-10} (compare Veley, T., 1908, **93**, 2114; 1909, **95**, 758).
W. G.

Quinaketones. ADOLF KAUFMANN and PAUL HAENSLE (Ber., 1917, **50**, 702—705. Compare A., 1913, i, 1222).—When cinchoticine (originally "dihydrocinchotoxine") is treated with bromine in hydrobromic acid solution, it yields bromocinchoticine dihydrobromide, from which a *monohydrobromide*, m. p. 194—195°, has now been obtained by the application of the calculated quantity of sodium hydrogen carbonate. The free brominated base (I.) cannot be isolated, however, for the tendency to the closure of the quinuclidine ring is too strong. The product, cinchotinone ("hydrocinchoninone") II., forms a *hydriodide*, m. p. 196°, and the *hydriodide* of an iso-methiodide, yellowish-red leaflets or needles, m. p. 214—215°.



[Q = Quinolyl.]

Cinchotinone may also be brominated in chloroform solution, the halogen replacing the hydrogen atom adjacent to the carbonyl group. *Bromocinchotinone* crystallises in yellow needles, m. p. 161—162°.
J. C. W.

Corydalis Alkaloids. XIV. *r*-Corydaline. J. GADAMER [and, in part, WALTER KLEE] (*Arch. Pharm.*, 1916, **254**, 295—305).—Gadamer and Wagner have shown (A., 1902, i, 307) that the reduction of dehydrocorydaline leads to the formation at times of an optically inactive corydaline, m. p. 158—159°, in addition to Ziegenbein's optically inactive corydaline, m. p. 135°. Later Gadamer and Haars produced evidence indicating that the latter is to be regarded as *r*-corydaline and the former as *r*-mesocorydaline (A., 1905, i, 462), the two compounds being stereoisomeric. The conditions have now been established under which either substance can be obtained at will. *r*-Corydaline alone is produced, but not quantitatively, when an aqueous solution of dehydrocorydaline hydrochloride is reduced by platinised zinc and dilute sulphuric acid on the water-bath; amongst the other products of the reaction is found a phenolic base, m. p. 220—224°, which exhibits the properties and colour reactions of *i*-corybulbine. Under milder conditions of reduction, by keeping an alcoholic solution of dehydrocorydaline hydrochloride with zinc dust and sulphuric acid for several days at the ordinary temperature until it is decolorised, a very good yield of nearly equal quantities of *r*-mesocorydaline and *r*-corydaline is obtained; the separation of the two bases is easily effected since *r*-mesocorydaline alone crystallises from an ethereal solution of the mixture.

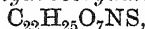
r-Mesocorydaline forms a hydrochloride containing $1\text{H}_2\text{O}$

(Gadamer and Haars state $2\text{H}_2\text{O}$, *loc. cit.*), m. p. 238—240° (decomp.) or 247—248° (anhydrous); *sulphate*, small crystals; *nitrate*, well-formed, anhydrous crystals, decomp. 207—208°; *aurichloride*, reddish-yellow needles, m. p. 191—192° (decomp.); and *platini-chloride*, amorphous.

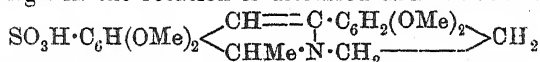
Although *r*-mesocorydaline has been resolved into active components (the *d*-form is not identical with natural *d*-corydaline), attempts to resolve *r*-corydaline have failed (Gadamer, A., 1911, i, 153). It can be sulphonated in the same way as natural *d*-corydaline (Gadamer and Wagner, *loc. cit.*) and yields *r*-corydaline-sulphonic acid, glistening leaflets, m. p. above 300°. This is easily resolved by means of brucine, calculated quantities of the acid and the base in warm dilute alcohol yielding on cooling *brucine l-corydalinesulphonate*, stout leaflets containing $4\text{H}_2\text{O}$. *l*-Corydaline-sulphonic acid also crystallises in leaflets and when neutralised by *N*/10-potassium hydroxide has $[\alpha]_D - 153.5^\circ$. Since the *d*-sulphonic acid obtained from natural corydaline has $[\alpha]_D + 150.3^\circ$ under the same conditions, the inactive corydaline, m. p. 135°, is indubitably proved to be *r*-corydaline.

r-Mesocorydalinesulphonic acid, rosettes of slender needles, is obtained in the same way as *d*-corydalinesulphonic acid (*loc. cit.*). It cannot be resolved by means of the brucine salt.

When *d*-corydalinesulphonic acid is boiled with an alcoholic solution of iodine the consumption of iodine corresponds with the removal of only two atoms of hydrogen (not of four, as the authors had anticipated) and *didehydrocorydalinesulphonic acid*,



colourless crystals with $5\text{H}_2\text{O}$, is obtained. This develops a magnificent bluish-green fluorescence in concentrated sulphuric acid and is strongly laevorotatory in solution. The significance of this change of sign in the rotation is discussed and the formula



is ascribed to the substance for reasons stated in the paper.

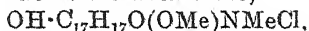
C. S.

Methyl Derivatives of Morphine. C. MANNICH (*Arch. Pharm.*, 1916, 254, 349—363).—According to the constitution of morphine proposed by Knorr and Pschorr, the alkaloid functions as a tertiary base, as a phenol, and as a secondary alcohol. Theoretically, therefore, one trimethyl, three dimethyl, and three monomethyl derivatives should be capable of existence. Four of these are already known and the remaining three are now described.

Although Pschorr and Dickhäuser's methylcodeine methiodide (A., 1911, i, 908) undergoes extensive decomposition by heating, the corresponding *methochloride*, $\text{C}_{20}\text{H}_{26}\text{O}_2\text{NCl}$, colourless crystals, m. p. 208° (*picrate*, yellow needles, m. p. 211—212°; *platinichloride*, yellow needles, decomp. about 215°), loses methyl chloride by heating under 2 mm. pressure and yields *morphine OO-dimethyl ether*, $\text{C}_{17}\text{H}_{17}\text{ON}(\text{OMe})_2$, prismatic or tabular crystals, m. p. 140—141°. This method of demethylating quaternary bases is unfortunately

not applicable to any other morphine derivative. A second method of preparing the same dimethyl ether is the following. Morphine oxide or codeine oxide is shaken with a large excess of *N*-sodium hydroxide and methyl sulphate at 0° , the solution is faintly acidified with hydrochloric acid and treated with concentrated aqueous potassium iodide, and the crystalline substance obtained, m. p. about 253° (doubtless the hydriodide of morphine oxide dimethyl ether), is heated at about 80° with sulphurous acid and a little sodium hydrogen sulphite, and the solution is basified and extracted with ether, whereby morphine OO-dimethyl ether, identical with that mentioned above, is obtained. It has not been converted into thebaine by oxidation, but yields methylcodeine methiodide by treatment with chloroform and methyl iodide, and its hydrochloride in aqueous solution is reduced by hydrogen and palladinised charcoal to *dihydromorphine dimethyl ether hydrochloride*, $C_{17}H_{19}ON(OMe)_2 \cdot HCl \cdot 3H_2O$, small plates, m. p. about 116° .

Morphine methoxymethyl ether, $C_{17}H_{17}ON(OH)(O \cdot CH_2 \cdot OMe)$, colourless needles, m. p. $94-96^{\circ}$, obtained by treating a suspension of the sodium derivative of morphine in cold chloroform, with chloromethyl ether, is insoluble in alkali hydroxides, does not give a coloration with ferric chloride, but instantly develops a violet coloration (the morphine-formaldehyde reaction) with concentrated sulphuric acid. It is stable towards alkalis, but is converted by dilute acids into morphine, formaldehyde, and methyl alcohol. The *sulphate*, $2C_{10}H_{23}O_4N \cdot H_2SO_4$, forms crystals containing $10H_2O$, and the *methiodide* tufts of needles, m. p. 225° (decomp.). When the ether is shaken with an excess of *N*-sodium hydroxide and methyl sulphate at 0° and the product is treated with cold, concentrated aqueous potassium iodide, *morphine O-methoxymethyl O-methyl ether methiodide*, $OMe \cdot CH_2 \cdot O \cdot C_{17}H_{17}O(OMe)N \cdot MeI$, crystals, decomp. about 253° , is obtained. The corresponding *methochloride*, $C_{21}H_{25}O_4NCl$, decomp. about 200° , is converted by warming with sulphurous acid and a little sodium hydrogen sulphite into *heterocodeine methochloride*,



colourless crystals, m. p. above 270° , which does not give a violet coloration with concentrated sulphuric acid but develops a blue coloration with aqueous ferric chloride. The methochloride cannot be converted into *heterocodeine* (this is the name given by the author to the monomethyl ether of morphine methylated at the secondary alcoholic group), which is obtained, however, by the following method. Morphine methoxymethyl ether is gently warmed with hydrogen peroxide, and the resulting syrup, which doubtless contains an amino-oxide, is treated with *N*-sodium hydroxide and methyl sulphate at 0° , and the resulting solution is acidified with dilute sulphuric acid and treated with concentrated aqueous potassium iodide solution; the precipitate is collected and warmed with sulphurous acid for two days, whereby *heterocodeine*, $OH \cdot C_{17}H_{17}ON(OMe)$, crystals, m. p. 242° , is obtained, which is isolated as the *hydrochloride*, prisms containing $2H_2O$, m. p. 102° .

Heterocodeine is soluble in alkali hydroxides, develops a blue coloration with ferric chloride and a reddish-violet coloration with formaldehyde and sulphuric acid, and is shown to be a true derivative of morphine, not of *iso*- or ψ -codeine, by its conversion by diazomethane into morphine OO-dimethyl ether. C. S.

Preparation of Cephaeline Amyl Ethers and Salts thereof. J. W. MEADER (Brit. Pat., 105722, 1916; addition to Brit. Pat., 103881; from *J. Soc. Chem. Ind.*, 1917, **36**, 615. Compare this vol., i, 348).—*Cephaeline amyl ethers* other than the *iso*amyl ethers, which form the subject of the principal patent, are produced by treating cephaeline with an alkali metal and an amyl haloid. The process is the same as that described in the principal patent, and the product has similar properties. H. W.

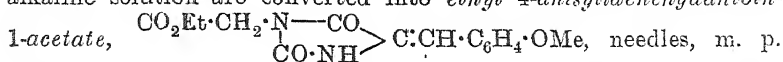
Preparation of 3-Nitrocarbazole and its Halogen Derivatives. AKTIEN GESELLSCHAFT FÜR ANILINFABRIKATION (D.R.-P., 295817; from *J. Soc. Chem. Ind.*, 1917, **36**, 542).—3-Nitrocarbazole and its halogen derivatives are obtained by treating carbazole or its halogen substitution products with about two molecules of nitric acid (10%). H. W.

Preparation of Arylalkylhydantoins. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat., 105719; from *J. Soc. Chem. Ind.*, 1917, **36**, 615).—Arylalkylhydantoins of the general formula
$$\begin{array}{c} \text{Ar} \\ \diagup \\ \text{Alk} > \text{C} < \begin{array}{l} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{array} \end{array}$$
 are produced in the same manner as other hydantoins or cyclic ureides, starting from arylalkylaminoacetic acids, or causing the latter to be produced during the process. They are therapeutically valuable on account of their hypnotic action. Eight methods of preparation are described. Thus, ethyl α -amino- α -phenylbutyrate (20 parts) is neutralised with dilute hydrochloric acid and a concentrated solution of potassium cyanate (8 parts) is added. After a short time the solution is boiled, when *phenylethylhydantoin*, m. p. 198°, separates. It forms soluble alkali and alkaline-earth salts. Alternatively, cyanophenylacetamide is transformed into *phenylethylecyanoacetamide*, m. p. 120°, by the action of ethyl bromide in the presence of alcoholic sodium ethoxide; the latter is added to a solution of sodium hypobromite, heated to 40°, and cooled; after treatment with sodium hydrogen sulphite solution, phenylethylhydantoin is precipitated by acidifying with hydrochloric acid. *Phenylmethylhydantoin*, *piperonylmethylhydantoin*, and *p-chlorophenylethylhydantoin* have m. p. 193°, 192—193°, and 212° respectively. H. W.

Hydantoins. XXXIX. Synthesis of the Polypeptide-hydantoin; Tyrosylglycine-hydantoin. TREAT B. JOHNSON and DOROTHY A. HAHN (*J. Amer. Chem. Soc.*, 1917, **39**, 1255—1266. Compare Johnson and Bates, A., 1916, i, 504).—It has already

been suggested that the fibroin molecule may contain "polypeptide-hydantoin," and as fibroin on hydrolysis yields a large proportion of glycine and tyrosine, the preparation of tyrosylglycine-hydantoin was undertaken.

4-Anisylidenehydantoin (Wheeler and Hoffmann, A., 1911, i, 499) and its reduction product, 4-anisylhydantoin (Johnson and Nicolet, A., 1912, i, 585), when treated with ethyl chloroacetate in alkaline solution are converted into *ethyl 4-anisylidenehydantoin-1-acetate*,



and *ethyl 4-anisylhydantoin-1-acetate*, needles, m. p. 138° , respectively; the latter product is also obtainable by reduction of the former in alcoholic solution with tin and hydrochloric acid, and both esters are hydrolysable to the corresponding *acids*, plates, m. p. 271° , and prisms, m. p. 166° (*potassium salt*, plates, decomp. near 260°), respectively. The anisylidenehydantoinacetic acid appeared to be capable of existence in an *isomeric* form, the aqueous solution under certain conditions depositing a substance of similar external appearance, but of no m. p. below 315° . When treated in hot alcoholic solution with a bimolecular proportion of potassium hydroxide, ethyl 4-anisylhydantoin-1-acetate was converted into *s-glycine-p-methoxyphenylalaninocarbamide*,

$\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, plates, m. p. 161° (decomp.) (*dipotassium salt*), which readily yields 4-anisylhydantoin-1-acetic acid on heating with hydrochloric acid.

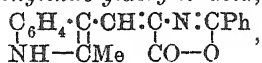
The polypeptide-hydantoin, namely, *4-hydroxybenzylhydantoin-1-acetic acid*,

$\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{N}-\text{CO} \begin{array}{c} \text{CO}\cdot\text{NH} \end{array} > \text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, rosettes of compact crystals, m. p. $217-218^\circ$ (*ethyl ester*, needles, m. p. 195°), was obtainable from 4-anisylidenehydantoin-1-acetic acid or its ester by reduction with hydriodic acid or with tin and hydrochloric acid, and also from 4-anisylhydantoin-1-acetic acid and its ester by heating with hydrobromic acid; the latter process gave rise to the *ethyl ester*, needles, m. p. 195° , as an intermediate product, the methoxy-group undergoing scission before the ester group. When hydrolysed with hydrochloric acid, 4-hydroxybenzylhydantoin-1-acetic acid or its ester gave rise to ammonia, carbon dioxide, and tyrosine, whilst treatment with alcoholic potassium hydroxide yielded the *dipotassium salt* (compact crystals) of unstable *s-tyrosineglycinecarbamide*,

$\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, which readily underwent reconversion into the polypeptide-hydantoin.
D. F. T.

Synthesis of *r*-2-Methyltryptophan. GEORGE BARGER and ARTHUR JAMES EWINS (*Biochem. J.*, 1917, 11, 58-63).—The first step in the synthesis of this methyltryptophan is the preparation of 2-methylindole-3-aldehyde from 2-methylindole, which is accomplished by Gattermann's hydrocyanic acid method with a 75% yield (compare Plancher and Ponti, A., 1907, i, 341). From this

aldehyde the synthesis closely follows that of tryptophan by Ellinger and Flamand (A., 1907, i, 737). The *azlactone* of α -benzoylamino- β -2-methylindolylacrylic acid,



is formed by the interaction of the aldehyde and hippuric acid in the presence of anhydrous sodium acetate and acetic anhydride, and on recrystallisation from glacial acetic acid or chloroform gives orange-yellow prisms which sinter at 202° and melt at 211°. The corresponding acid, α -benzoylamino- β -2-methylindolylacrylic acid, $\text{C}_{19}\text{H}_{16}\text{O}_3\text{N}_2$, crystallises from 70% alcohol in pale yellow, prismatic needles, m. p. 221—222°. The acid is reduced by dissolving in alcohol and treating with sodium, and the benzoyl group then removed by boiling after the addition of a little water. The

resulting γ -2-methyltryptophan, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} - \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H} \\ | \\ \text{NH} - \text{CMe} \end{array}$

crystallises with 1MeOH from methyl alcohol and ether in colourless prisms, m. p. 263—273°, according to the rate of heating. It gives a strong reaction with triketohydrindene hydrate. With excess of bromine water a precipitate is produced, but not a coloration, which indicates that the bromine reaction of natural tryptophan probably consists of an attack on the α -carbon atom of the indole ring. The reactions with Hopkins and Cole's reagent and with glyoxylic acid are given only by relatively strong solutions of methyltryptophan. Methyltryptophan has a sweet taste and yields a picrate, $\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, orange-red plates, from methyl alcohol and light petroleum, m. p. 173°.

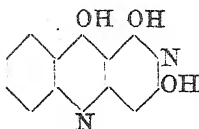
In a feeding experiment, the urine of a dog after the administration of 0.5 gram of methyltryptophan contained an indole derivative, but neither kynurenic acid nor a similar substance. The authors are therefore unable to draw definite conclusions as to the mechanism of the production of kynurenic acid from tryptophan (compare Asayama, A., 1916, i, 860).

H. W. B.

Synthesis of 1:3:10-Trihydroxybenzo-2:5-naphthyrindine [1:3:10-Trihydroxy-2:5-naphthadiazine] and its Conversion into Kynurenic Acid. ST. VON NIEMENTOWSKI and ED. SUCHARDA (*J. pr. Chem.*, 1916, [ii], 94, 193—227).—Details are given of the best conditions for preparing glutazine from ethyl β -amino- β -hydroxy- γ -carbamylbutyrate by the method of von Pechmann and Stokes (1885). The mother liquors are found to contain the sodium salt, $\text{C}_5\text{H}_4\text{O}_3\text{NNa} \cdot 2\text{H}_2\text{O}$, of 2:4:6-trihydroxypyridine, orange, sandy, crystalline powder, so that the yield of this substance, from this source and from the hydrolysis of the glutazine, amounts to 55% of that theoretically obtainable. The trihydroxypyridine forms a *diacetyl* derivative, faintly yellow needles, m. p. 247°.

When a mixture of anthranilic acid (2 mols.) and glutazine or 2:4:6-trihydroxypyridine (1 mol.) is heated from 130° to 160° during three hours, only one product is obtained. The condensa-

tion follows the same course in acetic acid or neutral aqueous solution at the b. p., but fails in alkaline or in mineral acid solution. The formation of only one product is quite unexpected, since phloroglucinol yields at least three products by condensation with anthranilic acid. The product, $C_{12}H_8O_3N_2$, yellow, metallic needles, m. p. 370° , is regarded as 1:3:10-trihydroxybenzo-2:5-naphththyridine (annexed formula), since it yields 4-hydroxy-2-methylquinoline quantitatively by heating with hydrochloric acid, D 1.1, at 245° . The substance, which is the first representative of this class of compound, has pronounced acid properties (*potassium* salt, $C_{12}H_7O_3N_2K, 3\frac{1}{2}H_2O$, yellow needles, becoming dirty violet at 110°),



but its salts with mineral acids are unstable and easily hydrolysed (*hydrochloride*, $C_{12}H_8O_3N_2 \cdot HCl, 2H_2O$, golden-yellow needles). It forms an *acetyl* derivative, $C_{12}H_7O_3N_2 \cdot Ac$, yellow, microcrystalline plates, m. p. about 373° , *dibenzoyl* derivative, cream-coloured, microcrystalline plates containing $1C_5H_5N$ (the substance is prepared in the presence of pyridine), and *p-nitrobenzeneazo*-derivative, $C_{18}H_{11}O_5N_5$, yellowish-bronze, microcrystalline powder, becoming brick-red when powdered, m. p. 336° . The dibenzoyl derivative loses its pyridine at $117-122^\circ$ and becomes flesh-coloured, and then cream-coloured again; when heated in a capillary tube, it softens at 160° and has m. p. about 205° . By crystallisation from a cold benzene solution, the dibenzoyl derivative separates in yellowish-white, microcrystalline needles, which do not contain pyridine, have m. p. 235° , and are changed into the preceding, pyridine-containing form by solution in pyridine and precipitation with water. These phenomena are probably to be explained by the change from the trihydroxy- to the triketo-structure.

The trihydroxybenzonaphththyridine forms a *sulphonic acid*, $C_{12}H_7O_3N_2(SO_3H)$, aggregates of golden- or brownish-yellow prisms containing $4H_2O$, which carbonises at $350-390^\circ$.

According to the experimental conditions, three different products are obtained by the oxidation of 1:3:10-trihydroxybenzo-2:5-naphththyridine by potassium permanganate. By triturating a mixture of the two solids for ten minutes, the chief product is 4-hydroxyquinoline-2:3-dicarboxylimide, $OH \cdot C_6H_4N \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} NH$, golden-yellow leaflets, m. p. 379° (decomp.). A by-product of the oxidation is 4-hydroxyquinoline-3-carboxylamide-4-carboxylic acid, $OH \cdot C_6H_4N(CO_2H) \cdot CO \cdot NH_2$, faintly yellow, stout needles containing $1H_2O$ or colourless, anhydrous lamellæ, which is also obtained by hydrolysing the preceding imide with aqueous ammonia, and is the chief product when the oxidation of the trihydroxybenzonaphththyridine is effected by cold alkaline potassium permanganate (three atomic proportions of oxygen). It loses carbon dioxide at 200° or by prolonged boiling with glacial acetic acid, and is converted into 4-hydroxyquinoline-3-carboxylamide (*kynurenamide*), $OH \cdot C_6H_4N \cdot CO \cdot NH_2$, m. p. 283° (slight decomp.), which crystallises

from water or dilute acids or aqueous ammonia in colourless needles containing $1\text{H}_2\text{O}$, and from glacial acetic acid in glistening, apparently octahedral crystals containing $1\text{C}_2\text{H}_4\text{O}_2$. Kynurenamide is converted by boiling 20% hydrochloric acid or by cold nitrous acid into kynurenic acid, which yields kynurine above its m. p. or by heating with hydrochloric acid, D 1'1, at 200° . Kynurine, and also 1:3:10-trihydroxybenzo-2:5-naphthyridine, are oxidised to oxalylanthranilic (kynuric) acid by an excess of hot alkaline potassium permanganate.

By treatment with a hot solution of potassium hypobromite, 4-hydroxyquinoline-3-carboxylamide-2-carboxylic acid gave, not the expected 3-amino-4-hydroxyquinoline-2-carboxylic acid, but 3-bromo-4-hydroxyquinoline-2-carboxylic acid, $\text{C}_{10}\text{H}_6\text{O}_3\text{NBr}$, yellow needles with $1\text{H}_2\text{O}$, which softens at about 120° , loses carbon dioxide at 200° , and is thereby converted into 3-bromo-4-hydroxyquinoline, cream-coloured leaflets, m. p. 282° .

C. S.

Preparation of Chloro-derivatives of N-Dihydro-1:2:1':2'-anthraquinoneazine [Indanthrene]. CHEMISCHE FABRIK GRIESHEIM ELEKTRON (D.R.-P., 296192; from *J. Soc. Chem. Ind.*, 1917, **36**, 591).—Indanthrene is treated with sulphur chloride in an inert medium at temperatures below 100° . The resulting dichloro-derivative is materially faster to chlorine than indanthrene blue G.C.D., and nearly as fast as indanthrene blue G.C. The product is in a finely divided state, and is suitable for the manufacture of bright-coloured pigments.

H. W.

Preparation of Polychloro-substitution Products of N-Dihydro-1:2:1':2'-anthraquinoneazine [Indanthrene]. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 296841; from *J. Soc. Chem. Ind.*, 1917, **36**, 591).—Indanthrene is suspended in an inert organic liquid and treated with an excess of chlorine at temperatures not materially exceeding 40° . The products, particularly the tri- and tetra-chloro-substitution derivatives, are characterised by their brightness of shade and resistance to the action of chlorine.

H. W.

Tautomerism. The Tautomeric Reactions of 1-Phenyl-4:5-dihydro-1:2:4-triazole-5-one 3-Methyl Sulphone and its Salts with Diazomethane and with Alkyl Haloids. H. A. LUBS and S. F. ACREE (*J. Amer. Chem. Soc.*, 1917, **39**, 950—961. Compare A., 1907, i, 258).—The sodium and silver salts of 1-phenyl-4:5-dihydro-1:2:4-triazole-5-one 3-methyl sulphone have been acted on by various alkyl haloids and the relative amounts of the isomeric O- and N-esters formed determined. The alkyl haloids used were methyl and ethyl iodide and allyl bromide. In all these reactions it was found that any salt and alkyl haloid in a given solvent gave a constant ratio of esters independent of the temperature and duration of the reaction, this indicating that the isomerides are formed by independent side reactions and not in accordance with the series of changes, salt \rightarrow O-ester \rightarrow N-ester, which applies

to the simple amides (compare Wheeler, A., 1903, i, 293). Any alkyl haloid gave a higher percentage of N-ester from the sodium salt than from the silver salt, and any given salt gave a higher percentage of N-ester from methyl iodide than from ethyl iodide.

[With LAWSON WILKINS.]—Allyl bromide and the silver sulphone salt gave the same ratio of esters at 25° and 100°, this case thus differing from that of silver 1-phenyl-4-methylurazole and allyl iodide, where partial conversion of the O-ester into the N-ester occurs at 100° (compare following abstract).

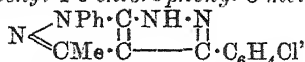
Diazomethane reacts with the sulphone giving the O-ester and the N-ester, the two esters being formed by reactions of the same apparent order. W. G.

The Rearrangement of 3-Allyloxy-1-phenyl-4-methylurazole. J. M. JOHNSON and S. F. ACREE (*J. Amer. Chem. Soc.*, 1917, **39**, 962—965. Compare preceding abstract).—At 60°, or below, the sodium, silver, or mercury salt of 1-phenyl-4-methylurazole each gives with allyl iodide its own ratio of N-ester and O-ester independent of the temperature and duration of the reaction. At 100°, however, in the case of the silver salt, there is a partial decomposition of the O-ester by the allyl iodide with the formation of some N-ester, the ratio thus being increased in the direction of N-ester formation W. G.

Application of Friedel and Crafts' Ketone Synthesis to Pyrazoles. A. MICHAELIS and C. A. ROJAHN (*Ber.*, 1917, **50**, 737—753).—5-Chloro-4-benzoyl-1-phenyl-3-methylpyrazole is a typical aromatic ketone, which is particularly interesting because of its behaviour towards hydrazine hydrate, whereby a dipyrazole derivative may be obtained (A., 1903, i, 288). The method originally employed for the preparation of this ketone involves several reactions and is not suited to the production of homologues, but it is now found that the Friedel and Crafts' synthesis may be applied to 5-chloro-1-phenyl-3-methylpyrazole with good results, except in the case of those derivatives of benzoyl chloride in which there are strongly electro-negative groups in the meta- or para-positions. A number of such ketones and typical derivatives, especially dipyrazoles, are now described.

The yield of 5-chloro-4-benzoyl-1-phenyl-3-methylpyrazole obtained by the new method is about 60—75% of the parent chloropyrazole.

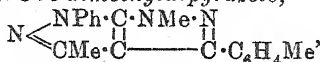
5-Chloro-4-o-chlorobenzoyl-1-phenyl-3-methylpyrazole forms stout, highly refractive crystals, m. p. 110°, and reacts with hydrazine hydrate to give 1-phenyl-4-o-chlorophenyl-3-methyldipyrazole,



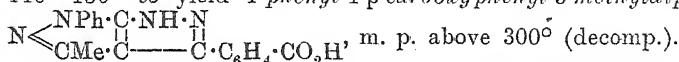
which crystallises in silky leaflets or needles, m. p. 251°. 5-Chloro-4-p-bromobenzoyl-1-phenyl-3-methylpyrazole crystallises in colourless needles, m. p. 124°, and 1-phenyl-4-p-bromophenyl-3-methyldipyrazole has m. p. 246°. In the case of 5-chloro-4-m-bromobenzoyl-1-phenyl-3-methylpyrazole, m. p. 70°, the yield is exceedingly small.

5-Chloro-4-p-toluyol-1-phenyl-3-methylpyrazole crystallises in very long needles, m. p. 86°, b. p. 220°/100 mm., and 1-phenyl-4-p-tolyl-

3-methyldipyrzole has m. p. 226°. The latter may be methylated to 1-phenyl-4-p-tolyl-3:6-dimethyldipyrzole,



which forms long, refractive needles, m. p. 167°, and the former oxidised by means of 40% chromic acid in the cold to 5-chloro-4-p-carboxybenzoyl-1-phenyl-3-methylpyrazole, needles, m. p. 195°. This acid forms a sodium salt, a silver salt, and a methyl ester, m. p. 162°, and the sodium salt reacts with hydrazine hydrate at 140—150° to yield 1-phenyl-4-p-carboxyphenyl-3-methyldipyrzole,



The corresponding derivatives in the ortho-series are: 5-chloro-4-o-toluoxy-1-phenyl-3-methylpyrazole, m. p. 84°, b. p. 243—245°/12 mm.; 1-phenyl-4-o-tolyl-3-methyldipyrzole, leaflets, m. p. 217°; 5-chloro-4-o-carboxybenzoyl-1-phenyl-3-methylpyrazole (methyl ester, very long needles, m. p. 122°); 1-phenyl-4-o-carboxyphenyl-3-methyldipyrzole, m. p. 232° (decomp.) (hydrazide, m. p. decomp. 233°).

Attempts were also made to obtain 4-acyl derivatives by applying the Friedel and Crafts' method to 5-chloro-3-methylpyrazole, but the only group to be attacked was the imino-group, 1-acyl compounds being formed. These are also obtained by the action of the acyl chlorides on the sodium salt of the pyrazole. 5-Chloro-1-benzoyl-3-methylpyrazole, $\text{N} \begin{array}{c} \diagup \text{NBz} \cdot \text{CCl} \\ \diagdown \text{CMe} \cdot \text{CH} \end{array}$, has m. p. 36°, b. p. 302°, and the

1-acetyl compound, m. p. 15°, b. p. 201—202°.

5-Amino-4-benzoyl-1-phenyl-3-methylpyrazole (*loc. cit.*) forms a hydrazone, $\text{N} \begin{array}{c} \diagup \text{NPh} \cdot \text{C} \cdot \text{NH}_2 \\ \diagdown \text{CMe} \cdot \text{C} \cdot \text{CPh} \cdot \text{N} \cdot \text{NH}_2 \end{array}$, yellow needles, m. p. 276—277°, and a dark red dye, m. p. 164°, when diazotised and coupled with β -naphthol.

J. C. W.

Synthesis of a Naphthatetrazine from Ethyl Succinylsuccinate and Dicyanodiamide. ARTHUR W. DOX (*J. Amer. Chem. Soc.*, 1917, **39**, 1011—1013).—Ethyl succinylsuccinate condenses with dicyanodiamide in aqueous sodium hydroxide to give 2:7-dicyanoamino-4:9-diketotetrahydro-1:3:6:8-naphthatetrazine, which, like its allied compounds, is characterised by its insolubility, infusibility, and general inertness.

W. G.

The Constitution of Internal Diazo-oxides (Diazophenols).

II. GILBERT T. MORGAN and HENRY PHILIP TOMLINS (*T.*, 1917, **111**, 497—506. Compare *T.*, 1915, **107**, 657).—No authenticated case of the formation of an internal diazo-anhydride derived from a *m*-aminophenol has yet been observed. In an attempt to produce such a meta-diazo-oxide the authors have made comparative experiments on the diazotisation of 3-amino-4-hydroxy-, 3-amino-5-hydroxy-, and 2-amino-4-hydroxy-benzenesulphonic acids. The diazo-derivative of the first-named acid, namely, benzene-2-diazo-1-oxide-4-sulphonic acid, $\text{N}_2 \begin{array}{c} \diagup \text{O} \\ \diagdown \end{array} \text{C}_6\text{H}_3 \cdot \text{SO}_3\text{H}$, or $\text{N}_2 \begin{array}{c} \diagup \text{O} \\ \diagdown \end{array} \text{C}_6\text{H}_3 \cdot \text{SO}_3\text{H}$, is a yellow

solid, which has already been obtained in solution by Bennewitz (this Journ., 1874, 374), but was erroneously described as the corresponding meta-compound. 3-Amino-5-hydroxybenzenesulphonic acid gives a colourless diazo-derivative (described by Bennewitz under the belief that the parent compound contained the amino- and hydroxyl-groups in the ortho-position to one another) resembling "diazobenzenesulphonic acid" (benzene-1-diazonium-4-sulphonate); this colourless product gives rise to coloured salts with the alkali or alkaline earth metals and with organic bases such as pyridine, piperidine, dibenzylamine, or brucine, the change being represented structurally by the formulæ $\text{OH} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{SO}_3 \\ \diagup \text{N}_2 \end{smallmatrix}$, and

$\begin{smallmatrix} \text{N}_2 \\ \diagdown \text{O} \end{smallmatrix} > \text{C}_6\text{H}_3 \cdot \text{SO}_3\text{R}$, or $\text{N}_2 \gg \text{C}_6\text{H}_3 \cdot \text{SO}_3\text{R}$, where R represents the basic radicle.

2-Amino-4-hydroxybenzenesulphonic acid also yields a colourless diazo-derivative, namely, 4-hydroxybenzene-2-diazonium-

1-sulphonate, $\text{HO} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{SO}_3 \\ \diagup \text{N}_2 \end{smallmatrix}$; this is less stable than its isomerides

and decomposes readily with liberation of nitrogen and formation of resorcinol-4-sulphonic acid, which then couples with the undecomposed portion of the diazonium compound with production of an azo-dye.

For experimental details, the original should be consulted.

D. F. T.

Product of Oxidation of *p*-Phenylenediamine (Ursol) by Hydrogen Peroxide. (Bandrowski's Base, Tetra-aminodiphenyl-*p*-azophenylene). A. HEIDUSCHKA and E. GOLDSTEIN (*Arch. Pharm.*, 1916, 254, 584—625).—In view of the use of a solution of hydrogen peroxide and *p*-phenylenediamine as a hair-dye, the reaction between these two substances, which has been cursorily examined by Erdmann (A., 1904, i, 935), has been thoroughly studied by the authors in order to ascertain the influence on the yield of tetra-aminodiphenyl-*p*-azophenylene of the following factors: (1) concentration of the *p*-phenylenediamine; (2) amount of hydrogen peroxide (2.98% solution); (3) time of the reaction; and (4) the temperature. In all the experiments a constant amount of 10% sodium carbonate solution, which was found to have no appreciable effect on the oxidation, was added to destroy the acidic impurities in the hydrogen peroxide. In all cases, substances other than Bandrowski's base are produced in larger or smaller amounts. The theoretical yield of Bandrowski's base is calculated in accordance with the equation $3\text{C}_6\text{H}_4(\text{NH}_2)_2 + 3\text{H}_2\text{O}_2 = \text{C}_{18}\text{H}_{18}\text{N}_6 + 6\text{H}_2\text{O}$.

The influence of (1) is found by allowing aqueous solutions of *p*-phenylenediamine (1—4%) to react with 2.98% hydrogen peroxide (10% in excess of the theoretical quantity) for twenty-four hours at 18—20°. The yields of base are 6—16.3%, nothing approaching the amounts (80—90%) claimed by Erdmann ever

having been obtained. The yield does not increase proportionally to the concentration.

The influence of (2) is found by keeping the reaction mixture containing 1.88% of *p*-phenylenediamine at 18—20° for twenty-four hours. With amounts of hydrogen peroxide increasing from 0.636 mol. to 3.636 mols. (per 1 mol. of *p*-phenylenediamine), the yield of Bandrowski's base increases proportionally from 4.7% to 27.7%. With yet larger amounts of hydrogen peroxide, impure products are obtained, 5 mols. of hydrogen peroxide yielding a black, non-crystalline mass.

The effect of time is found by prolonging the period of reaction of the solutions used in the experiments under (1). After seven days, the yield of oxidation product is 30—40%, and after three months only 60%, of the theoretical.

Rise of temperature accelerates the reaction at the expense of the purity of the product, but its effect is unimportant within the range of temperature which the skin can endure.

The preceding results are represented graphically.

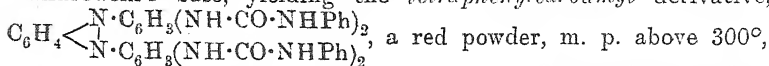
It has been found that *p*-phenylenediamine in solution can be estimated by precipitation as *p*-benzoquinonedichloroimide by an excess of calcium hypochlorite solution, and it is thus shown that in the preceding experiments, after removal of the Bandrowski's base, the filtrates contain 40—60% of unchanged *p*-phenylenediamine after twenty-four hours, about 50% after thirty days, and appreciable amounts after three months; in addition, about 20% of the diamine has been oxidised to unisolable products.

Despite certain differences in properties, Erdmann states (*loc. cit.*) that the base obtained by oxidising *p*-phenylenediamine with hydrogen peroxide is identical with the tetra-aminodiphenyl-*p*-azophenylene $\left[\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \cdot \text{C}_6\text{H}_4(\text{NH}_2)_2 \\ \text{N} \cdot \text{C}_6\text{H}_4(\text{NH}_2)_2 \end{array} \right]$ obtained by Bandrowski (A., 1894, i, 236) by oxidising an ammoniacal solution of *p*-phenylenediamine by atmospheric oxygen or a solution of its hydrochloride by potassium ferricyanide. The authors prepare the base by oxidising an ammoniacal solution of *p*-phenylenediamine by aqueous potassium ferricyanide (whereby it is obtained rapidly and almost quantitatively), and find that after purification with pyridine it has m. p. 239—240° (Bandrowski gives 230—231°; Erdmann, 242—243°; Willstätter, 238—238.5°) and no water of crystallisation (compare Bandrowski and Erdmann, *loc. cit.*). The appearance of the base differs in different methods of preparation, being obtained sometimes in very slender, bronze leaflets, at other times in dark brown crystals, and yet again in large, dark red prisms. Estimations of the nitrogen by the Dumas method give the expected results; those obtained by the Kjeldahl method are 2—3% too low.

The base forms a *sulphate*, $\text{C}_{18}\text{H}_{18}\text{N}_6 \cdot 2\text{H}_2\text{SO}_4$, brown powder, m. p. above 290°, and *platinichloride*, $\text{C}_{18}\text{H}_{18}\text{N}_6 \cdot 2\text{H}_2\text{PtCl}_6$, blackish-grey, crystalline powder, and reacts in pyridine solution with acid anhydrides or chlorides on the water-bath to form tetra-acyl deriv-

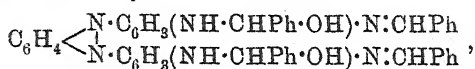
atives; *tetrapropionyl*, red crystals, m. p. 273° (decomp.); *diphthaloyl*, brownish-red needles, m. p. 295° (decomp.); and *tetrabenzoyl*, brown crystals softening at 295°. Thioacetic acid has a simultaneous reducing and acetylating action on Bandrowski's base in pyridine solution, a colourless substance, m. p. above 300°, being obtained, which appears to be identical with Bandrowski's tetra-acetylaminodiphenyl-*p*-phenylenediamine.

Phenylcarbimide and ethyl chloroformate react normally with Bandrowski's base, yielding the *tetraphenylcarbamy*l derivative,



a red powder, m. p. above 300°, and the *tetracarbethoxy*-derivative, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \cdot \text{C}_6\text{H}_5(\text{NH} \cdot \text{CO}_2\text{Et})_2 \\ \text{N} \cdot \text{C}_6\text{H}_5(\text{NH} \cdot \text{CO}_2\text{Et})_2 \end{array}$ pale red crystals, m. p. 284—285°, respectively.

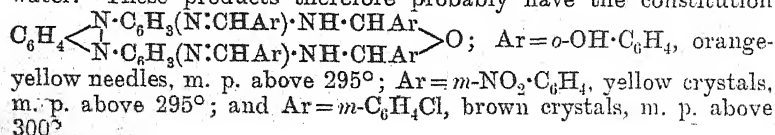
The behaviour of the base towards aldehydes is very diverse. It does not react with aliphatic aldehydes. When heated on the water-bath with benzaldehyde ($1\frac{1}{2}$ —2 times the theoretical amount) in pyridine solution it yields a substance,



yellow needles, m. p. 254°, which is converted at 260° into the

tetrabenzylidene derivative, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \cdot \text{C}_6\text{H}_5(\text{N} \cdot \text{CHPh})_2 \\ \text{N} \cdot \text{C}_6\text{H}_5(\text{N} \cdot \text{CHPh})_2 \end{array}$ a brown

powder, m. p. above 300°. *p*-Hydroxybenzaldehyde behaves in a similar manner, yielding a corresponding additive condensation derivative, $\text{C}_{46}\text{H}_{38}\text{O}_6\text{N}_6$, yellowish-white crystals, m. p. above 302°, but the following aldehydes yield condensation products only: cinnamaldehyde yields the *tetracinnamylidene* derivative, $\text{C}_{54}\text{H}_{42}\text{N}_6$, orange-yellow needles, m. p. 271°; anisaldehyde, the *tetraanisylidene* derivative, $\text{C}_{50}\text{H}_{42}\text{O}_4\text{N}_6$, straw-yellow needles, m. p. above 300°, and also a *dianisylidene* derivative, $\text{C}_{34}\text{H}_{30}\text{O}_2\text{N}_6$, crimson crystals, m. p. above 300°; *p*-chlorobenzaldehyde, the *tetra-p-chlorobenzylidene* derivative, $\text{C}_{46}\text{H}_{30}\text{N}_6\text{Cl}_4$, colourless, crystalline powder, m. p. above 302°; vanillin, the *tetравanillylidene* derivative, $\text{C}_{50}\text{H}_{42}\text{O}_8\text{N}_6$, yellowish-white, crystalline powder, m. p. 301° (decomp.); and piperonal, the *tetrapiperonylidene* derivative, $\text{C}_{50}\text{H}_{34}\text{O}_8\text{N}_6$, faintly yellow leaflets, m. p. 278°, becoming brown at 255°. Bandrowski's base condenses with *p*-nitrobenzaldehyde to form the *di-p-nitrobenzylidene* derivative, $\text{C}_{32}\text{H}_{24}\text{O}_4\text{N}_8$, a dark red, crystalline meal, m. p. above 295°, and with salicylaldehyde, *m*-nitrobenzaldehyde, and *m*-chlorobenzaldehyde to form condensation products derived from 1 mol. of the base and 4 mols. of the aldehyde by the elimination of 3 mols. of water. These products therefore probably have the constitution



Bandrowski's base can be diazotised in the usual way, but the diazotised solution cannot be made to couple with amines or phenols and does not yield characteristic products by boiling.

C. S.

Transformation of ψ -Globulin into Euglobulin. W. N. BERG (*J. Agric. Research*, 1917, **8**, 449—456).—Analytical data are given which indicate the transformation of ψ -globulin into euglobulin in four serums which were heated at 60° for thirty minutes in the presence of ammonium sulphate at one-third saturation. The four serums used were two anthrax, one diphtheria, and one tetanus. In the anthrax and diphtheria serums the conversion was considerable, but in the tetanus serum it was so small as to indicate that the transformation does not take place in all serums. The use of the centrifuge was found greatly to improve the separation of the globulin precipitates from their filtrates.

W. G.

Chemistry of the Colouring Matter of the Blood. I. ZALESKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1337—1653).—A complete and critical account of this subject.

T. H. P.

The Optimum Reaction in Tryptic Digestion. I. J. H. LONG and MARY HULL (*J. Amer. Chem. Soc.*, 1917, **39**, 1051—1059. Compare Michaelis and Davidschn, A., 1911, i, 1051).—The tryptic digestion of fibrin and casein has been followed in liquids of known composition with definitely varied hydrogen-ion concentration, the range being $P_H=2.37$ —11.86. In each case there is a marked change in the hydrogen-ion concentration of the solutions on the addition of the protein. In the acid solutions the acidity is reduced, and in the alkaline solutions the alkalinity is reduced. In the case of fibrin, the equilibrium is at about $P_H=6.5$, and with casein at about $P_H=4.9$. The optimum hydrogen-ion concentration for the action of trypsin on fibrin is $C_H=10^{-8}$ to 5×10^{-9} , and for casein 3×10^{-6} to 5×10^{-7} . Further, in the case of casein, the digestion proceeds at a degree of acidity much greater than that for the beginning of the fibrin digestion. It is probable that for each type of protein there is a distinct range for the optimum activity.

W. G.

Theory of the Oxidation of Benzidine in its Significance for Peroxydase Investigations. GERTRUD WOKER (*Ber.*, 1917, **50**, 672—677. Compare this vol., i, 62).—Polemical. A reply to Madelung (this vol., i, 285).

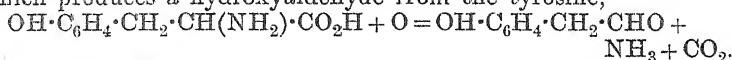
J. C. W.

[Aldehyde Hypothesis of the Peroxydases.] GERTRUD WOKER (*Ber.*, 1917, **50**, 677—679. Compare this vol., i, 61).—Polemical. A reply to van der Haar (this vol., i, 301).

J. C. W.

Tyrosinase, a Mixture of Two Enzymes. T. FOLPMERS (*Biochem. Zeitsch.*, 1916, **78**, 180—190).—Experiments are quoted which tend to show that the formation of melanin from tyrosinase

is due to two ferment actions. The first is that of a deamidase, which produces a hydroxyaldehyde from the tyrosine,



The second ferment causes a further oxidation of the aldehyde (or its condensation product with ammonia) to a melanin. In the case of phenylglycine, the author succeeded in actually demonstrating the presence of a deamidase, in that he isolated benzaldehyde in the form of its *p*-nitrophenylhydrazone (m. p. 192—193°) when he treated this substance with the juice of *Euphorbia lathyris* and other plants. An analogous condensation product of *p*-nitrophenylhydrazine and aldehyde was apparently obtained when tyrosine was treated in a similar way, but not in sufficient amount for complete identification.

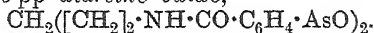
S. B. S.

Esters of Aromatic Arsenic Compounds (*p*-Benzarsinic Acid) and Amino-acids and Higher Alcohols. ERNST SIEBURG (*Arch. Pharm.*, 1916, 254, 224—245).—In the series $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{As}(\text{OH})_2$, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}$, $(\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4)_2\text{As}_2$, and $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{AsH}_2$ the first, second, and fourth members are already known; the remaining two have now been prepared. *p*-Benzarsine oxide [*p*-carboxyphenylarsine oxide], $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}$, an amorphous powder which is extremely soluble in ether, is obtained by acidifying a solution of *p*-benzarsine iodide in aqueous sodium carbonate. When boiled with water, it is converted into *p*-benzarsenious acid, colourless needles, which is insoluble in ether. The oxide, which is at least ten times more poisonous than the hydrate, can be kept for at least eight days in a moderately concentrated aqueous solution of sodium hydroxide or carbonate at 0° without any appreciable diminution of its toxicity. *Phenylarsine-p-carboxylic acid*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{AsH}_2$, colourless prisms, m. p. 79—80°, is prepared by reducing a methylalcoholic solution of *p*-benzarsinic acid with hydrochloric acid (D 1·19) and zinc dust, the product being removed by distillation with steam. In the moist state it is very sensitive to atmospheric oxygen, immediately becoming yellow and changing apparently to *p*-arsenobenzoic acid.

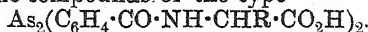
In connexion with his discussion (A., 1916, i, 777) of the action in the organism of preparations containing arsenic, the fact that *p*-arsenobenzoic acid injected into the animal organism is eliminated partly in the form of benzoylglycine-*p*-arsinic (hippuroarsinic) acid is important as showing that arsenic compounds are capable of reacting in the organism under certain conditions with the degradation products of the albumin molecule. The author has now prepared and examined a number of such compounds of amino-acids and aromatic arsenic compounds.

p-Benzarsinic acid is produced almost quantitatively by heating *p*-tolylarsinic acid with nitric acid (D 1·2) for three hours at 170° in a sealed vessel. The *p*-tolylarsinic acid is conveniently prepared by the interaction of diazotised *p*-toluidine and sodium arsenite in alkaline solution. This reaction of Bart gives a very poor yield

when it is applied to the direct production of *p*-benzarsinic acid from *p*-aminobenzoic acid. *p*-Benzarsinic acid is converted by a modification of Fourneau and Oechsli's method (A., 1912, i, 928) into *p*-dichloroarsinobenzoyl chloride, which reacts with the following amino-acids in the presence of aqueous sodium hydrogen carbonate to form, after acidification of the resulting solutions, the following arsine oxides: with alanine, *benzoylalanine-p-arsine oxide*, $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}$; with phenylalanine, *benzoylphenylalanine-p-arsine oxide*; with tyrosine, *benzoyltyrosine-p-arsine oxide* (in this case 2*N*-sodium hydroxide must be used instead of sodium hydrogen carbonate in order to prevent benzoylation of the hydroxyl group); with leucine, *benzoylleucine-p-arsine oxide*; with aspartic acid, *benzoylaspartic acid p-arsine oxide*; with glutamic acid, *benzoylglutamic acid p-arsine oxide*; and with pentamethylenediamine, *dibenzoylpentamethylenediamine-pp'-diarsine oxide*,




The preceding substances are all very similar in their properties. They are amorphous, white powders which do not exhibit sharp m. p.'s, are easily soluble in methyl or ethyl alcohol and in alkali hydroxides, carbonates, or hydrogen carbonates, and do not dissolve in dilute hydrochloric acid; the oxygen of the AsO-group cannot be replaced by halogens or sulphur. They are oxidised to the corresponding arsinic acids by careful treatment with hydrogen peroxide in alkaline solution, and are reduced by sodium amalgam to arseno-compounds of the type



The latter are amorphous, yellow substances without definite m. p.'s, but the arsinic acids are crystalline: *benzoylalanine-p-arsinic acid*, $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$, cubic crystals; *benzoylphenylalanine-p-arsinic acid*, needles; *benzoyltyrosine-p-arsinic acid*, long, pointed plates; *benzoylleucine-p-arsinic acid*, needles; *benzoylaspartic p-arsinic acid*, hone-shaped crystals; and *benzoylglutamic p-arsinic acid*, cubic crystals.

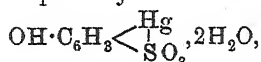
p-Dichloroarsenobenzoyl chloride reacts easily and smoothly with the higher alcohols. The reaction is effected in benzene solution in the presence of pyridine at the ordinary temperature, and finally on the water-bath. Myricyl alcohol yields *myricyl benzoate p-arsine oxide*, $\text{C}_{80}\text{H}_{61}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}$, which in acetone solution is oxidised to the *arsinic acid*, $\text{C}_{37}\text{H}_{67}\text{O}_5\text{As}$, pointed leaflets, by hydrogen peroxide, and is reduced to the *arseno-compound*, $\text{C}_{74}\text{H}_{130}\text{O}_4\text{As}_2$, yellow powder, by phosphorous acid. Cholesterol yields *cholesteryl benzoate p-arsine oxide*, $\text{C}_{34}\text{H}_{48}\text{O}_3\text{As}$, colourless powder; the *arsinic acid*, $\text{C}_{34}\text{H}_{50}\text{O}_5\text{As}$, forms pointed needles, and the *arseno-compound*, $\text{C}_{68}\text{H}_{96}\text{O}_4\text{As}_2$, is a yellow powder. The arsinic acid does not give Windaus's digitonin reaction. C. S.

***p*-Sulphomethylaminophenylarsinic Acid.** J. ABELIN (*Biochem. Zeitsch.*, 1916, **78**, 191–196).—The substance, which has the constitution $\text{SO}_3\text{H}\cdot\text{CH}_2\cdot\text{NH}$  $\text{AsO}(\text{OH})_2$, is an *N*-substituted derivative of atoxyl. It is prepared by treating the

sodium salt of *p*-aminophenylarsinic acid with formaldehyde sodium bisulphite in concentrated solution and precipitating from this mixture the free acid with hydrochloric acid. The free acid forms needles which decompose at 148°. The substance is much less toxic than atoxyl, and its action on trypanosomes is apparently much weaker. S. B. S.

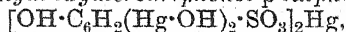
Mercuriation Products of Phenol-*p*-sulphonic Acid. E. RUPP and A. HERRMANN (*Arch. Pharm.*, 1916, 254, 500—509).—

Gautrelet states that hydrargyrol has the formula $\text{OH}\cdot\text{C}_6\text{H}_3\text{SO}_3\text{Hg}$, is brownish-red in colour, and is soluble in water. The authors, working according to his instructions, obtained a colourless substance which is insoluble in water and is not hydrargyrol. The clear solution obtained by heating an aqueous solution of phenol-*p*-sulphonic acid with yellow mercuric oxide (1 or 2 mols.) on the water-bath soon deposits a colourless, gelatinous precipitate (the filtrate contains a small quantity of a substance,



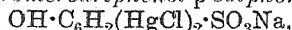
colourless, rhombic crystals, when 1 mol. of mercuric oxide is used), which forms a heavy, indistinctly microcrystalline powder when dried. This is 2:6-dihydroxymercuriphenol-*p*-sulphonic acid, $\text{OH}\cdot\text{C}_6\text{H}_2(\text{Hg}\cdot\text{OH})_2\cdot\text{SO}_3\text{H}$, which is insoluble in water, but dissolves in concentrated aqueous sodium hydroxide, forming the disodium salt, $\text{ONa}\cdot\text{C}_6\text{H}_2(\text{Hg}\cdot\text{OH})_2\cdot\text{SO}_3\text{Na}$, rhombic crystals containing $5\text{H}_2\text{O}$; from the solution carbon dioxide precipitates the sodium salt, $\text{OH}\cdot\text{C}_6\text{H}_2(\text{Hg}\cdot\text{OH})_2\cdot\text{SO}_3\text{Na}$. Sodium 2:6-diacetato-mercuriphenol-*p*-sulphonate, $\text{OH}\cdot\text{C}_6\text{H}_2(\text{Hg}\cdot\text{OAc})_2\cdot\text{SO}_3\text{Na}$, colourless, microcrystalline powder, is obtained by heating a concentrated aqueous solution of sodium phenol-*p*-sulphonate with mercuric acetate on the water-bath; it readily loses acetic acid, and by prolonged boiling with water the preceding sodium salt is obtained.

*Mercuric 2:6-dihydroxymercuriphenol-*p*-sulphonate,*



a heavy, colourless, amorphous powder, is obtained by heating an aqueous solution of phenol-*p*-sulphonic acid with $2\frac{1}{2}$ mols. of mercuric oxide or acetate on the water-bath for a long time.

*Sodium 2:6-dichloromercuriphenol-*p*-sulphonate,*



colourless needles containing $2\text{H}_2\text{O}$, is obtained (1) by adding a solution of sodium 2:6-diacetato-mercuriphenol-*p*-sulphonate in aqueous sodium hydroxide to a hot solution of sodium chloride containing a moderate quantity of acetic acid; (2) by dissolving sodium 2:6-dihydroxymercuriphenol-*p*-sulphonate in hot, concentrated sodium chloride solution; (3) by heating a solution of mercuric chloride (2 mols.), sodium acetate (2 mols.), and sodium phenol-*p*-sulphonate (1 mol.) on the water-bath; and (4) by adding sodium chloride to a suspension of mercuric oxide in a solution of

sodium phenol-*p*-sulphonate. It is converted into picric acid by 20% nitric acid; into 2:6-dichloro-*p*-benzoquinone by passing chlorine into its suspension in water, and into potassium sozoiodol ($\text{OH}\cdot\text{C}_6\text{H}_2\text{I}_2\cdot\text{SO}_3\text{K}$) by warming with iodine and a solution of potassium iodide.

C. S.

Physiological Chemistry.

Effect of Alcohol on the Respiration and the Gaseous Metabolism in Man. HAROLD L. HIGGINS (*J. Pharm. Exper. Ther.*, 1917, 9, 441—472).—The author describes the effects on respiration and gaseous metabolism of the administration to men of doses of 30 c.c. and 45 c.c. of ethyl alcohol (suitably diluted with water and flavoured, but not as alcoholic beverages). An endeavour was made to secure complete rest during the experiments by carrying them out before breakfast, the men lying down and remaining as motionless as possible throughout the two to three hours' period of observation. Control experiments were made in which the flavoured water administered was free from alcohol.

In many cases the alcohol appeared to produce very little effect; in a few instances only was there a fall in the alveolar carbon dioxide tension denoting an increase in the sensitiveness of the respiratory centre. Definite actions on the bronchial muscles, affecting the "dead space," or on the heat production, as indicated by the consumption of oxygen, could not usually be detected. The rate of respiration is not altered, neither is the type of respiration changed. In half the experiments, a slight acceleration of the pulse rate occurred. The increased power of voluntary inhibition of the respiration after taking alcohol, described by Mackenzie and Hill (*A.*, 1910, ii, 1079), is confirmed.

In the majority of cases, there is a fall in the respiratory quotient after small doses of alcohol. From the figures obtained, it is calculated that about 3.5 c.c. of alcohol per hour are oxidised in the body and the rate of oxidation is independent of the amount of alcohol taken.

H. W. B.

New Method for the Estimation of the Total Volume of Blood in Man. MAX DE CRINIS (*Zeitsch. physiol. Chem.*, 1917, 99, 131—149).—The method consists in estimating the percentage of protein in the serum of the blood before and after the intravenous injection of 500 c.c. of physiological salt solution. If the volume of the blood is V and A and B are the percentages of protein in the serum before and after injection respectively, then $(V + 500)/V = A/B$.

In its application to the human subject, the percentage of protein in the serum is estimated by means of the refractometer, and corrections are made for the effect of dilution on the refractive power

of the non-protein substances in the blood and for the volume of urine excreted by the kidney during the time occupied by the experiment.

The results are of the same order as those found by other methods. The volume of blood in normal men varies between 3300 and 5600 c.c., or 1/17 to 1/13 of the body-weight. This new method may be of clinical value, since the volume of blood of an individual is found in ordinary circumstances to vary only within small limits during periods extending over several weeks. The actual quantity of blood required for the estimations is also small, being not more than 16 c.c. H. W. B.

The Calculation of the Hydrion Concentration of the Blood from the Amount of its Free and Bound Carbon Dioxide, and the Combination of the Blood with Oxygen considered as a Function of the Hydrion Concentration. K. A. HASSELBALCH (*Biochem. Zeitsch.*, 1916, **78**, 112—144).—The first dissociation constant of carbonic acid in the presence of sodium hydrogen carbonate, $k_2 = [H^+] \times \delta \times [\text{Bicarb}]/[\text{CO}_2]$. If 10^{-p_K} be substituted for K , then $-p_K = -p_H + \log \delta + \log [\text{Bicarb}]/[\text{CO}_2]$, when δ = dissociation grade of the bicarbonate.

If $p_{K_1} = p_K + \log \delta$, then $p_H = p_{K_1} + \log [\text{Bicarb}]/[\text{CO}_2]$.

A series of experiments was carried out, in which the determination of p_H was made electrometrically of a known solution of sodium hydrogen carbonate in the presence of air containing varying amounts of carbon dioxide. As the absorption coefficient of water for carbon dioxide is known, the value of $[\text{CO}_2]$ at various temperatures can be calculated. An apparatus is described for saturating the bicarbonate solution with air containing carbon dioxide of known tension and for transferring the saturated liquid to the hydrogen electrode. If the value p_H is once determined for solutions with varying values of $[\text{Bicarb}]$ and $[\text{CO}_2]$, it is, conversely, possible, by determining the amounts of free and combined carbon dioxide in a solution, to determine p_H . A similar series of experiments was carried out with blood, in which, also, the absorption coefficient for carbon dioxide is known. It was found that the determination of free and bound carbon dioxide affords a more accurate determination of the hydrion concentration than the direct electrometric measurement. It was found to be normally under 40 mm. tension of carbon dioxide $10^{-7.33}$. Incidentally, the dissociation constant of carbonic acid was determined, and found to be greater at 38° than at 18°, which is in accordance with Julius Thomsen's thermochemical measurements. The bound carbon dioxide of the blood is exclusively in the form of a hydrogen carbonate. With diminishing carbon dioxide tensions the amount of bound carbon dioxide also diminishes, chiefly on account of the fact that oxyhæmoglobin becomes a stronger acid as the reaction becomes more alkaline. Oxyhæmoglobin (more than the other proteins), on account of its marked ampholytic character, protects the blood against changes in the hydrion concentration. This rôle is played both when acids are added or the temperature is changed,

and is of special physiological importance in that, in the circulation of the blood, as the fluid becomes more saturated with carbon dioxide, the acid action of the oxyhæmoglobin diminishes owing to its conversion into reduced hæmoglobin. The relationship established in one case by Peters and Barcroft between p_H and the constant k in Hills's formula ($y/100 = kx^{2.5}/1 + kx^{2.5}$, where y = percentage saturation with oxygen, x = oxygen pressure, and k varies with hydron concentration and carbon dioxide tension) has been reinvestigated and found to hold as regards human blood in many cases. It does not hold so accurately in the cases of blood of ox, pig, and pigeon. In pregnancy, the value of the reduced p_H (that is, p_H under 40 mm. tension of carbon dioxide) is about 0.03 below the normal.

S. B. S.

The Ammonia Content of Blood. V. HENRIQUES and E. CHRISTIANSEN (*Biochem. Zeitsch.*, 1916, **78**, 165—179).—By the use of a method involving the principle of that employed by Folin and Denis, the amount of ammonia in the blood from various animals was found to be about 0.27 mg. per 100 c.c. There is no marked increase in the case of the dog after a meat diet. After injection of large amounts of ammonium salts, there was an increase for a short time to about 0.9 mg., but the amount soon became normal. Neither extirpation of the kidneys nor ligature of both ureters causes an increase in the amount of ammonia in the blood. On the other hand, the amount of urea and residual nitrogen increases daily. The amino-nitrogen increases in the first day, but does not exceed about 60 mg. per 100 c.c.

S. B. S.

Urea as a Source of the Ammonia in the Blood. GEORGE D. BARNETT and THOMAS ADDIS (*J. Biol. Chem.*, 1917, **30**, 41—46).—There is a marked increase in the amount of ammonia in the blood of rabbits after the administration of urea by the mouth, directly into the intestine, or intravenously. Death from ammonia poisoning frequently follows such injections. These results suggest that normally ammonia may be derived from urea in the animal organism.

H. W. B.

Calcium Content of Human Blood. HENRY LYMAN (*J. Biol. Chem.*, 1917, **30**, 1—3. Compare this vol., ii, 271).—The amount of calcium in human blood varies but little in health and disease. The average of the analyses of fifty-three samples taken under normal and pathological conditions was 6.1 mg. of calcium per 100 c.c. of blood for the males and 7.1 mg. for females. Even in cases of advanced uræmia, where the total nitrogen was extremely high, and in those of hæmorrhage, the calcium figures were normal.

H. W. B.

Residual Reducing Power of the Blood. W. GRIESBACH and H. STRASSNER (*Zeitsch. physiol. Chem.*, 1917, **99**, 224—228. Compare A., 1913, ii, 1082; Schumm, A., 1916, ii, 454).—Polemical. The authors maintain that the very small amount of so-called

residual reducing substance found by Schumm in normal blood and urine after fermentation with yeast is without significance, because it falls within the limits of experimental error of the method of estimation employed. H. W. B.

The Normal Reaction of the Intestinal Tract. J. H. LONG and FREDERICK FENGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1278—1286).—Earlier investigators of the reaction of the fluid in the small intestine have made use of the ordinary indicators; in the present investigation the hydrogen-ion concentration has been determined by electrometric measurement. Experiments were made with men, hogs, calves, lambs, and a dog, and the conclusion is drawn that in the human small intestine the reaction may vary from distinctly acid to slightly alkaline, whilst with the animals mentioned notable variations are also found, the upper portion of the intestine being most strongly acidic, whilst the lower portion may be alkaline. A considerable quantity of gas, mainly nitrogen with smaller quantities of carbon dioxide and oxygen, was found in the intestines of the hog. D. F. T.

Effect of High Temperatures on the Nutritive Value of Foods. ALBERT G. HOGAN (*J. Biol. Chem.*, 1917, **30**, 115—123. Compare A., 1916, i, 861).—The nutritive value of a protein is not impaired by heating to a high temperature in an autoclave. The deleterious effect observed when foods such as wheat and other grains are similarly subjected to heat is probably due to the destruction of indispensable accessory substances. H. W. B.

The Physiological Evaluation of the Esters of Fatty Acids.
I. Ethyl Esters. JOHANNES MÜLLER and HANS MURSCHAUSER (*Biochem. Zeitsch.*, 1916, **78**, 63—96).—The experiments were carried out on a dog with the ethyl esters of the fatty acids of beef. To a dog were administered for a preliminary period a diet of meat and fat, followed by a diet in which the fat was replaced by an equivalent amount of ethyl esters, and this was followed by another period in which the original fat and meat diet was resumed. The caloric value of the ingesta and egesta was determined, and also the intake and output of carbon and nitrogen. During each period, the respiratory exchanges were determined by a Zuntz-Loewy apparatus over a period of six hours each day. The fat and unsaponifiable substances in the faeces were also estimated. The main result indicated that whereas the fat was utilised to the extent of 94%, the ethyl esters were utilised only to the extent of 75%. During the diet of the ethyl ester, there was a certain amount of degradation of body protein. Ethyl palmitate was utilised to a greater extent (75%) than the stearate (64%). It is claimed that ethyl esters can be used to replace fats in a war diet. S. B. S.

Supplementary Dietary Relationship between Leaf and Seed as Contrasted with Combinations of Seed with Seed. E. V. MCCOLLUM, N. SIMMONDS, and W. FITZ (*J. Biol. Chem.*, 1917, **30**, 13—32.)—The results of these experiments on rats indicate that

it is difficult, if not impossible, to obtain even a moderate amount of growth over an extended period on a diet restricted to the seeds of plants, because of their inadequate content of salts, particularly of sodium and calcium. The leaf, however, contains a large proportion of salts and is especially rich in salts of sodium and calcium. Mixtures of leaf and seed are therefore more efficient than mixtures of seeds as a diet for growing animals. Moreover, the leaves of some plants, lucerne, for example, are several times richer in "fat-soluble A" than are the wheat, oat, and maize kernels. Certain small seeds, such as flax and millet seed, have approximately the same value as the leaf in this respect, and when incorporated with inorganic salts in sufficient amount with wheat, oats, or maize constitute a diet which is adequate to meet the needs of the growing animal.

H. W. B.

The Effect of the Ingestion of Aluminium on the Growth of the Young. J. T. LEARY and S. H. SHERB (*J. Amer. Chem. Soc.*, 1917, **39**, 1066—1073. Compare Kahn, *Biochem. Bull.*, 1911, **1**, 235, and Steele, *Amer. J. Physiol.*, 1911, **28**, 94).—Aluminium, when added in the form of aluminium hydroxide to the diet of young puppies, caused a marked increase in the faecal phosphates and a decrease in the amount excreted in the urine, accompanied by a decrease in the urinary acidity. There was also a decrease in the nutritional value of the diet when aluminium was added to it. The addition of aluminium hydroxide in varying amounts to the diet of young rats appeared to have no great effect on their growth, an ill-effect only being observed in one case. Absorption of aluminium occurred with the dogs and the rats, the liver being the seat of the greatest deposition.

W. G.

Mechanism of Cytolysis in Echinoderm Eggs. II. A. R. MOORE (*J. Biol. Chem.*, 1917, **30**, 5—11. Compare this vol., i, 185).—The experiments carried out with eggs of the sea-urchin (*loc. cit.*) have been repeated with those of the starfish, *Asterias forbesii*. The graphs derived from the experimental results indicate that the rate of cytolysis of starfish eggs is not constant, but depends on the chemical state of the egg, which in turn is determined by the age of the egg or the extent to which certain oxidations have taken place in it.

Treatment of starfish eggs with isotonic solutions of the chlorides of barium, strontium, calcium, and magnesium does not accelerate the rate of cytolysis in the manner observed with sea-urchin eggs. On the contrary, a slight inhibitory action is observed in each case.

H. W. B.

Genesis of Carbamide. I. Can Muscular Tissue Generate Carbamide? UGO LOMBRISO (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 569—573).—Blood circulating in functioning muscular tissue may undergo a marked increase in its content of carbamide. The addition of amino-acids does not constitute a necessary or even favourable condition for such increase; indeed, in some instances

in which a large proportion of amino-acid was added to the blood and a considerable percentage of it disappeared during the circulation, no increase of carbamide was observed. The greatest increase in the amount of carbamide in the blood was obtained when the muscular tissue and the blood employed were taken from a dog previously fed with meat.

T. H. P.

Biochemistry of Silicic Acid. MAX GONNERMANN (*Zeitsch. physiol. Chem.*, 1917, **99**, 255—296).—Silica is present in most tissues. The quantities, expressed in percentages of the total ash, are as follows: hair, 2 to 30; milk, 0.3 to 0.4; thymus, 8; adrenals, 7 to 16; blood corpuscles, 3; serum, 2 to 3; fibrin, 15 to 30; muscle, 2 to 4; intestine, 2 to 13. The author considers that silica is absorbed in the duodenum and excreted into the large intestine like iron compounds and other substances.

It appears that good effects have been observed to follow the administration of silicic acid in cases of tuberculosis. Most herbs contain considerable quantities of silica, and it is found on analysis that those herbs which are used by the country folk of Middle Europe for the cure of tuberculosis contain the largest percentages of silica.

H. W. B.

Concentration of Dextrose in the Tissues of Normal and Diabetic Animals. WALTER W. PALMER (*J. Biol. Chem.*, 1917, **30**, 79—114).—The author has estimated the concentration of dextrose in the muscle, liver, heart, kidney, spleen, pancreas, stomach, intestine, skin, lung, and eye tissues of normal and diabetic dogs and rabbits, under varying conditions. In a few instances the dextrose has been estimated in the bladder, parotid glands, oesophagus, uterus, tongue, diaphragm, thyroid, aorta, trachea, and brain. The tissues are removed as rapidly as possible from the body, and, after weighing, treated with boiling water to arrest enzymic action. The proteins are removed from the aqueous extract by colloidal iron and the dextrose estimated by Benedict's method.

The concentration of dextrose in the tissues is found to bear a more or less constant relation to the amount of sugar in the blood. It is invariably lower than the concentration of sugar in the blood, except in the liver, where the higher concentrations may be probably explained by rapid glycogenolysis. The largest amounts of sugar are found in the liver, the smallest quantity in the brain, the difference being largely accounted for by difference in vascularity. In the muscles the amount of dextrose is low, varying in normal animals between 0.04% when the dextrose in the blood is 0.10% and 0.41% when the dextrose in the blood reaches 1.05% after the intravenous injection of dextrose; whilst in diabetic animals it falls within the normal limits, even although the hyperglycæmia rises as high as 1.43%. The amount of dextrose found in either normal or diabetic tissues during hyperglycæmia is not influenced by variations in the method of producing the hyperglycæmia.

The chief difference in the results obtained from normal and

diabetic animals respectively is observed in the figures for the concentration of dextrose in striated muscle, which are invariably higher in the former class when the amount of dextrose in the blood is the same in both classes. The significance of this difference is not apparent.

H. W. B.

Human Adipocere. R. F. RUTTAN (*Trans. Roy. Soc. Canada*, 1917, [iii], 10, 169—170. Compare Ruttan and Marshall, this vol., i, 364).—The author has analysed specimens of adipocere of human origin, some of which were dry and firm and others soft and oily. The latter consist of immature adipocere and differ from the waxy variety in containing more oleic acid, proteins (soft connective-tissue and hyaline muscular fibres), and calcium soaps.

Human adipocere, whether mature or immature, shows a remarkable similarity in composition to the adipocere from the pig (*loc. cit.*). It is essentially composed of saturated fatty acids, glycerides being present in traces only. The two isomeric monohydroxystearic acids derived from oleic acid are invariably present, and the disappearance of unaltered oleic acid marks the final stage in the formation of mature adipocere.

Adipocere is regarded as the product of the hydrolysis of fats by water where the time factor and the concentration of the reacting water are almost indefinitely great and where the soluble product, glycerol, is rapidly removed. Bacterial and enzymic actions play a quite secondary part in the production of adipocere. The hard, waxy character of the mature substance is largely due to the presence of the two hydroxystearic acids.

H. W. B.

Comparative Investigations on the Excretion of Arsenic in Human Urine after Injection of Various Arsenical Medicaments. GEORG LOCKEMANN (*Biochem. Zeitsch.*, 1916, 78, 1—36).—As regards the rate of elimination of arsenic, the medicaments can be divided into two classes. In the first, which includes atoxyl and arsacetin, the greater part of the arsenic is excreted in the first two days after injection. The second class includes salvarsan, neosalvarsan, and arsenophenylglycine, and, after injection of these substances, arsenic is excreted only very slowly. There are differences in the rate of excretion of the various medicaments by male and female. Arsacetin is slightly degraded in the passage through the body, there being partial scission of the acetyl group with formation of atoxyl, and there is also a partial scission of the arsenic group. The substances containing the free amino-group were isolated by conversion into the diazo-derivative and the coupling of this with naphthylamine; the arsenic was estimated in the precipitate thus formed. The excretion of arsenic, both in male and female, follows a periodic course, more being excreted in the first, third, fifth day, etc., than in the intervening days. The rate of excretion diminishes after repeated doses. Particulars are given in detail as to the amounts of arsenic excreted at various intervals after various methods of injection (intramuscular, intravenous, and subcutaneous).

S. B. S.

Influence of the Protein Intake on the Excretion of Creatine in Man. W. DENIS [with ANNA S. MINOT] (*J. Biol. Chem.*, 1917, **30**, 47—51).—In five cases of Grave's disease it is shown that the amount of creatine excreted by these individuals is dependent on the intake of protein, being increased by high protein feeding and decreased or even eliminated by low protein feeding. It is suggested that a certain fraction of the ingested protein is transformed into creatine, transported to the muscles, and there absorbed. If so much creatine is manufactured that the muscles become supersaturated, creatine is excreted by way of the kidney. What constitutes supersaturation depends not only on the total mass of muscle, but on the capacity for creatine absorption possessed by those muscles. In childhood, in Grave's disease, and in other pathological conditions, the saturation point of the muscle for creatine is probably lower than in the normal person.

H. W. B.

Theory of Diabetes. VIII. Timed Intravenous Injections of Dextrose at Lower Rates. W. D. SANBURN and R. T. WOODYATT (*J. Biol. Chem.*, 1917, **30**, 155—173).—The authors describe experiments which indicate that the maximum rate at which dextrose can be continuously administered by intravenous injection to normal resting rabbits and dogs without causing gross glycosuria is about 0.85 gram per kilo. of body-weight per hour. This is termed the normal intravenous dextrose toleration limit. Within rather wide limits, the water administered simultaneously with the dextrose may be varied without appreciably affecting the rate of utilisation of the dextrose. Continued intravenous injection of dextrose at uniform rates between 0.9 and 2 grams per kilo. per hour leads to continued excretion of dextrose in the urine, also at uniform rates. The ratio of the intake to the output rate differs with different individuals. When the rate of injection is 1.8 to 2 grams per kilo. per hour, the excretion of dextrose per hour varies in different individuals from 2 to 10% of the amount injected. For any individual case the rate at which dextrose enters the blood determines the rate of utilisation and excretion of dextrose, regardless of the volume of the blood and urine or the concentration of dextrose in them.

H. W. B.

Formation of Lactic Acid and Acetoacetic Acid in the Livers of Diabetic Animals. G. EMBDEN and S. ISAAC (*Zeitsch. physiol. Chem.*, 1917, **99**, 297—321).—When dextrose is mixed with blood and perfused through the liver of a dog, it is transformed in part into lactic acid (Embden and Kraus, A., 1912, ii, 1070). The authors now find that similar perfusion of the liver of a depancreatized dog does not yield any lactic acid. Similar results are obtained with lævulose, although in a few cases small amounts of lactic acid are formed. When the diabetes is produced by phloridzin, the liver exerts a similar action, but in some cases dextrose is also partly converted into lactic acid. The livers of diabetic animals therefore fail to convert the simple carbohydrates into lactic acid,

but instead transform them into acetoacetic acid. In the experiments described by the authors it is noted that the amounts of lactic and acetoacetic acids produced vary inversely the one with the other.

H. W. B.

Identification of the Pentose in a Case of Pentosuria.

ALMA HILLER (*J. Biol. Chem.*, 1917, **30**, 129—134).—The melting point and mutarotation of the osazone prepared from the pentose in the urine in a case of pentosuria indicated the presence of *d*-xylose or a closely related pentose. The rotation of the concentrated urine excluded *d*-xylose, whilst the presence of a ketose was indicated by the bromine and colour tests. The pentose is therefore probably *d*-xyloketose.

H. W. B.

Reaction of Sera as a Factor in the Successful Concentration of Anti-toxic Sera by the Methods at Present in Use.

ANNIE HOMER (*Biochem. J.*, 1917, **11**, 21—39. Compare A., 1916, i, 614).—The author directs attention to the importance of controlling the reaction of an anti-toxic serum during the processes generally employed in its concentration. On the reaction of the serum depends not only the extent of the heat denaturation of the proteins of the serum, but also the successful precipitation of these proteins by ammonium sulphate. Unless the reaction is regulated, the necessary increased precipitation of the proteins cannot be ensured except by the addition to the serum of phenol, ether, chloroform, or similar substance which favours the destruction of antitoxin.

H. W. B.

The Astringent Action of Aluminium Salts, especially of the Formate. A. LOEWY and R. WOLFFENSTEIN (*Biochem. Zeitsch.*, 1916, **78**, 97—111).—Experiments are described which indicate the advantages of the use of the formate of aluminium as compared with the acetate. The former preparation is less irritant. It is best employed in solution which contains some sodium sulphate. Such a solution readily precipitates proteins and also produces contraction of the blood vessels.

S. B. S.

Inhibition of Digestion of Proteins by Adsorbed Tin.

B. C. GOSS (*J. Biol. Chem.*, 1917, **30**, 53—60).—Tin is readily adsorbed from solutions by coagulated proteins in amounts varying with the concentration according to the adsorption law of Freundlich. This adsorption takes place rapidly at first, and then continues to increase slowly for several days, presumably because of the time required for diffusion into the solid. The adsorption complex is extremely stable, and does not lose tin to a dilute acid or alkaline aqueous phase containing no tin, although the amount of tin in the solid may be as high as 50%. The presence of this tin, even in small amounts, interferes with the digestion of the protein by either pepsin or trypsin, but after a time solution of nearly all the protein occurs and only a small residue remains, which contains practically all the tin. It appears from these observations that it is only a part

of the protein, directly joined to the tin, of which the digestion is hindered, so that the effect of this retardation on the physiological value of tinned foods is probably small, since the total tin in such foods rarely exceeds 0.03%.

Prolonged digestion of the tin-protein complex with pepsin or trypsin does not lead to the solution of the tin. The activity of the enzymes also remains unimpaired, even after being one hundred hours in contact with the tin-protein complex. It is probable, therefore, that the tin present in canned foods escapes digestion and absorption in the animal body, and is therefore devoid of toxic action.

H. W. B.

Olfactology of the Methylbenzene Series. E. L. BACKMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 943—956).—A comparison has been made of the smallest quantities of benzene, toluene, xylene, ψ -cumene, and durene which can be detected by the olfactory organ. The quantity diminishes as the number of substituent methyl groups increases. The electrical charge produced by spraying equimolecular aqueous solutions of the above substances increases from benzene to xylene, and then diminishes for the higher homologues. Experiments on the olfactory properties of mixtures afford indications of compensation effects.

H. M. D.

Purine Metabolism after Poisons. JULIUS POHL (*Biochem. Zeitsch.*, 1916, **78**, 200—223).—The allantoin and uric acid output after administration (to rabbits or dogs) of the following substances was investigated: sodium chloride, bromide and iodide, calcium chloride, arsenious acid, lead carbonate, sodium malonate, sodium cyanide, benzene, bromobenzene, salicylic acid, sodium phenyleinchonate (alophan), pilocarpine, morphine, quinine, colchicine, adrenaline (*l* and *r*), thyroid gland. Increased output followed administration of arsenic, lead, sodium cyanide, bromobenzene, morphine (in all these cases of allantoin), colchicine (of uric acid), and adrenaline (of allantoin and uric acid).

S. B. S.

Chemistry of Vegetable Physiology and Agriculture

Decomposition of Protein Substances through the Action of Bacteria. R. H. ROBINSON and H. V. TARTAR (*J. Biol. Chem.*, 1917, **30**, 135—144).—The authors have studied the chemical changes that occur when a protein is acted on by certain organisms, *B. subtilis*, *B. mycoides*, and *B. vulgaris*, present in most soils. The percentages of nitrogen combined in various forms are estimated before and after bacterial action by Van Slyke's method.

The results indicate that all the forms in which nitrogen is combined are changed more or less by the action of the bacteria, and the end-product ammonia is formed. The monoamino-acid nitrogen and diamino-acid nitrogen of the protein are the chief sources of the ammonia produced, but the action of the bacteria is not confined to one particular form to the exclusion of the others. The rapidity of action varies greatly with different proteins, casein showing no further change after a few days, whilst gliadin continues to evolve ammonia after thirty days. The reason for the arrest of bacterial action has not been elucidated; it does not appear to be the formation of a toxic substance.

The changes observed indicate that the bacterial decomposition of proteins is effected by hydrolysis with the formation of the amino-acids and subsequent degradation with the liberation of ammonia.

H. W. B.

New Type of Chemical Change Produced by Bacteria. Conversion of Histidine into Urocanic Acid by Bacteria of the Coli-typhosus Group. HAROLD RAISTRICK (*Biochem. J.*, 1917, 11, 71—77).—Histidine is converted into urocanic acid (β -iminoazolyacrylic acid) in a medium consisting of Ringer's solution and histidine, by the following bacteria: *B. coli communis*, *B. typhosus*, *B. paratyphosus*, *B. enteritidis*, and *B. dysenteriae*. The change is represented by the equation $C_3H_3N_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H = C_3H_3N_2 \cdot CH:CH \cdot CO_2H + NH_3$.

H. W. B.

The Chemistry of the Fats of Tubercle Bacilli. MAX BÜRGER (*Biochem. Zeitsch.*, 1916, 78, 155—164).—Tubercle bacilli contain "cerolipoids" consisting partly of the homologous fatty acids of the series $C_nH_{2n}O_2$ from lauric to palmitic acids, and partly of high molecular alcohols of the formula $C_nH_{2n-2}O$ ($C_{15}H_{28}O$, $C_{19}H_{36}O$, and $C_{29}H_{56}O$).

S. B. S.

Chemical Conditions for the Development of the Reproductive Organs in some Yeasts. KENDO SAITO (*J. Coll. Sci. Imp. Univ. Tokyo*, 1916, 39, (3), 1—73).—The author has ascertained the action of various chemical agents on the development of spores by the following three yeasts: *Zygosaccharomyces manchuricus*, *Schizosaccharomyces octosporus*, and *Saccharomyces manchuricus*. The results indicate that the formation of spores only occurs when the medium in which the yeast cell is grown contains members of definite classes of substances.

Cells of *Zygosaccharomyces*, when transferred to pure water, do not form spores. If, however, a carbohydrate or similar substance is present, spores are formed, and this formation of spores occurs more readily in the presence of a simple monosaccharide than of a polysaccharide or carbohydrate derivative, such as dulcitol. The addition of a trace of potassium phosphate and Witte's peptone accelerates the production of spores. Ammonium salts, amino- and weak organic acids inhibit the reproductive process.

The concentration of the medium may be varied within wide limits without entirely arresting the development of spores. Thus, highly concentrated solutions up to 25% of potassium nitrate do not inhibit spore formation as much as an isotonic sodium chloride solution. The extreme limits of concentration applicable vary according to the previous training as regards food of the particular yeast employed, since yeasts, like bacteria and fungi, show adaptative capacity and may be gradually accustomed to unfamiliar circumstances.

Most yeasts require the withdrawal of food before spore formation can ensue. Schizosaccharomycetes is an exception to this rule, inasmuch as reproduction in this manner occurs in the unchanged medium, provided other conditions, such as temperature and degree of oxygenation, are favourable. H. W. B.

The Proteoclastic Ferments of Yeast and their Relationship to Autolysis. K. G. DERNBY (*Biochem. Zeitsch.*, 1917, 81, 109—208).—The author confirms the fact, originally discovered by Vines, that yeast contains more than one distinct proteoclastic ferment. He has succeeded in demonstrating the presence of three, which are analogous to, but differ in certain particulars from, the proteoclastic ferments of the animal organism. These ferments are: I. Yeast pepsin, which can degrade genuine proteins to peptones (but not further). Its optimal action is in a medium of $p_H=4-4.5$, whereas the animal pepsin acts best in a medium of $p_H=1.5$ (Sörensen). II. A yeast tryptase, which does not act on the proteins of yeast, but can degrade certain proteins, such as acid albumin, gelatin, caseinogen, into peptides and amino-acids. Its optimal action is in a medium of $p_H=7$, as compared with that of $p_H=8$, which is optimal for animal tryptase. III. A yeast ereptase, which readily degrades peptones and polypeptides into amino-acids and has an optimal action in a medium of $p_H=7.8$, which is very nearly the same as that of animal ereptase. It differs, however, from the latter in that its action is not markedly inhibited by neutral salts, whereas the animal ereptase is. A concentration of 0.5*N*-salt solution has little action on yeast ereptase, whereas the animal ereptase is inhibited by a concentration of 0.02*N*. The individual ions have apparently little action, as they act more or less alike, the diminution of the action of the ferment being controlled by the salt molecules as a whole. The autolysis of yeast is due to the successive action of the various ferments, and the maximal action takes place in a medium of $p_H=6.0$, which is midway between the optimal p_H concentrations for the yeast pepsin and the tryptase. Deamidases play only a subordinate rôle in the autolysis.

The method of investigation employed by the author consisted in following the course of degradation of yeast and other products in media with varying hydrogen-ion concentrations, both in the presence and absence of buffer solutions. In the absence of such solutions, the hydrion concentration changed during the course of the ferment action. The chief indication as to the presence of

various ferments was afforded in this case by estimating the total nitrogen, amino-peptide, and protein nitrogen in solutions of the autolysis mixture after varying intervals of autolysis. When no buffer mixture was present, the total nitrogen and amino-nitrogen continually increased, especially towards the end, whereas the peptide nitrogen first increased and then diminished, and the protein nitrogen first diminished (slightly) and then increased (slightly). The p_H changed during the reaction from 6.0 to 6.8. The results indicate that at the commencement the pepsin was chiefly active, whereas towards the end, in the more alkaline medium, the erepsin was most active.

The detailed action of the various ferments was also investigated by extracting them from yeast plasmolysed by chloroform in presence of calcium carbonate and submitting the extracts to dialysis against diminished pressure by a method recently described by Sørensen. The action of the pepsin was investigated on acid albumin by Sørensen's method, the unchanged protein being precipitated by Schjerner's stannous chloride solution, and also by the thymol-gelatin method of Palitzsch and Walbum (A., 1913, i, 112). The adaptation of this method is described in detail, and the fact that it indicated the presence of two optima of proteoclastic activity showed the presence of two ferments (tryptase and erepsin). The action of the erepsin on glycylglycine was investigated in detail and compared with that of animal erepsin. The reaction in the presence of a buffer mixture (phosphates) is unimolecular.

S. B. S.

The Presence of Emulsin-like Ferments Separable from the Cells of Bottom Yeast, and the Absence of Myrosin in Berlin Top and Bottom Yeast. CARL NEUBERG and EDUARD FÄRBER (*Biochem. Zeitsch.*, 1916, 78, 264—272).—The maceration juice of bottom yeast contains all three ferments which act on amygdalin (amygdalase, prunase, and oxynitrilase). β -Glucosides are also hydrolysed by the maceration juice of Munich bottom yeast. The myrosin ferment has been found neither in top nor bottom yeasts (free yeast and maceration juice of dried cells) of Berlin, and is also absent in dried Munich bottom yeast.

S. B. S.

Conditions of Activation of Washed Zymin and the Specific Function of Certain Cations in Alcoholic Fermentation. ARTHUR HARDEN (*Biochem. J.*, 1917, 11, 64—70).—Zymin and dried yeast, which have been inactivated by washing, can be activated by the addition of a pyruvate or acetaldehyde in the presence of dipotassium hydrogen phosphate. The potassium salt may be replaced by diammonium hydrogen phosphate, but not by the corresponding sodium salt. A specific difference in relation to alcoholic fermentation exists therefore between the ions of sodium on the one hand and of potassium and ammonium on the other. The presence of phosphate is also essential if activation is to occur.

These results appear to support the view that acetaldehyde is an intermediate product in alcoholic fermentation, and is reduced in

that process to alcohol by hydrogen liberated at a previous stage of the decomposition. H. W. B.

The Course of Alcoholic Fermentation in an Alkaline Medium. I. Cell-free Fermentation in Alkaline Solutions.

CARL NEUBERG and EDUARD FÄRBER (*Biochem. Zeitsch.*, 1916, **78**, 238—263).—In order to throw further light on the stages of alcoholic fermentation, experiments were carried out on the fermentation processes under atypical conditions. Normally, alcoholic fermentation takes place in an acid medium. It has been found by the authors that it will also take place in fairly strong alkaline media, provided that the alkali is added after fermentation has commenced. If it is added at the start, a precipitate is produced and fermentation is inhibited at low concentrations. This precipitate does not form in the presence of even larger amounts of alkali if the latter is added after once the fermentation has commenced. The experiments were carried out with maceration juice prepared from dried yeast, and the alkalis used were potassium and sodium carbonates, sodium sulphite, potassium metaborate, and potassium phosphate. Full fermentation took place in concentrations of 0.1 to 0.2*M* solutions of all these except the sulphite, with which a concentration of more than 0.02*M* was inhibitory in its action when these were added directly to the fermentation mixture. If the alkalis are added to the mixture after fermentation has started, the amounts tolerated are much higher (0.25—0.35*M* of the carbonates, etc., and 0.04—0.05 of sulphite). Experiments indicate that addition of alkalis to fermentation mixtures at the start do not exert their inhibitory action owing to removal of phosphates. Preliminary experiments indicate also that the products of fermentation in alkaline solution are not the same as the normal.

S. B. S.

Amygdalin as Nutriment for *Aspergillus niger*. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 922—927).—Earlier observations have shown that amygdalin is resolved into dextrose, benzaldehyde, and hydrogen cyanide by the extract from the cells of *Aspergillus niger*. This does not occur with the living cells, and in these circumstances the amygdalin is absorbed and assimilated by the mould which multiplies in the amygdalin solution. The experiments now described show that the organism will not develop if any considerable proportion of the amygdalin is already hydrolysed. The retardation is mainly due to the benzaldehyde, the action of which is possibly due to its ready solubility in fats and on the other hand to its rapid oxidation to benzoic acid. The behaviour of amygdalin and its products of hydrolysis towards the cells of *Aspergillus niger* affords an indication of a general method for the introduction of narcotic substances into living organisms. H. M. D.

Spontaneous Infection of a Saturated Potassium Chlorate Solution. H. J. WATERMAN (*Chem. Weekblad*, 1917, **14**, 514—515).—An account of a saturated solution of potassium chlorate which

did not crystallise, but after several weeks developed an unknown mould of the *Penicillium* type with green spores, and a red ferment.
A. J. W.

The Formation of Starch-like Substances by Moulds.

FRIEDRICH BOAS (*Biochem. Zeitsch.*, 1917, **81**, 80—86. Compare this vol., i, 370).—In the presence of mineral acids, *Aspergillus niger* can produce in the culture medium a substance giving the blue iodine reaction from glycerol and mannitol. It can also produce such a substance in fairly high concentrations from the following organic acids (the reaction being the most intense in the first-named acids) when they are used as the source of carbon in the medium: tartaric, citric, malic, succinic, and oxalic acids. The substance producing the iodine reaction tends to disappear after a certain interval.
S. B. S.

Utilisation of Certain Pentoses and Compounds of Pentoses by *Glomerella cingulata*. L. A. HAWKINS (*Amer. J. Botany*, 1915, **2**, 375—388; from *J. Soc. Chem. Ind.*, 1917, **36**, 663).—Previous investigators have shown that pentoses and pentosans are of some value as food for higher animals, but the latter appear to secrete no enzyme capable of hydrolysing pentosans, this transformation being probably effected by intestinal bacteria. Some of the invertebrates utilise pentoses readily, and can probably hydrolyse some pentosans. Pentoses have been found to be a good source of carbon for certain fungi, and there is evidence of decomposition of pentosans by enzymes secreted by fungi, although the products of such decomposition have apparently not been identified. In experiments with *Glomerella cingulata*, the author has found that this fungus can utilise dextrose, xylose, arabinose, xylan, or arabin as sole source of carbon. The three sugars are most efficiently utilised, xylose perhaps best of all. The pentosans are much less readily assimilated, and arabin less readily than xylan. The presence of a pentosanase in filtered aqueous extracts of the fungus mycelium was also demonstrated by the conversion of xylan into xylose, the latter being isolated in the crystalline form.
H. W.

Accessory Factors for Plant Growth. OTTO ROSENHEIM (*Biochem. J.*, 1917, **11**, 7—10).—An aqueous extract of Bottomley's bacterialised peat has remarkable growth-stimulating properties, which cannot be ascribed to the manurial value of the small amounts of nitrogenous and other substances present in it. The author suggests that the effect produced on plant growth is due to a substance or substances analogous to the vitamins or accessory substances in animal growth. Alcoholic or aqueous extracts of the treated peat give a precipitate with phosphotungstic acid, whilst similar extracts of ordinary peat or garden soil give only a faint opalescence or remain clear. The positive outfall of certain colour tests also indicates the presence of a substance similar to a vitamin in the treated peat.
H. W. B.

Influence of Manganese taken up by Plants on their Composition. PAUL EHRENBURG and OTTO NOLTE (*Landw. Versuchs-Stat.*, 1917, **90**, 139—145).—Direct experiment shows that increase of the manganese-content of plants to 0.1% produces no certain appreciable change in the composition of the incombustible matter of the plants.
T. H. P.

Viscosimetry of Living Protoplasm. FRIEDL WEBER (*Kolloid Zeitsch.*, 1917, **20**, 169—173).—A discussion of the methods which have been used in the determination of the viscosity of living protoplasm and of the factors which influence the magnitude of the viscosity.
H. M. D.

Formation of Starch [in Plants exposed] in the Spectrum. A. URSPRUNG (*Ber. Deut. bot. Ges.*, 1917, **35**, 44—69).—The author has investigated the formation of starch in the leaves of *Phaseolus multiflorus*, *Impatiens*, *Tropaeolum*, and *Coleus* at different positions of the spectra of the sun, moon, and various electric lamps. The extreme limits of wave-length within which starch is formed are found to be 760 and 330 μ . The latter value may be somewhat higher than the true minimum, since the experiments were made in the autumn, whereas June is the most suitable month. The region of starch-formation depends to some extent on the length of the exposure and on the nature of the source of light. The curves connecting the amount of starch formed with the wave-length exhibit a principal maximum and one or two subsidiary maxima.
T. H. P.

Deamidisation. KARL SCHWEITZER (*Biochem. Zeitsch.*, 1916, **78**, 37—45).—By means of the tyrosinase from potatoes, glycine can be degraded according to the equation $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + \text{O} = \text{H}\cdot\text{CHO} + \text{NH}_3 + \text{CO}_2$. The reaction takes place in the presence of an alkali (preferably calcium hydroxide), or of solutions of *p*-cresol; chlorophyll appears to accelerate the reaction. Formaldehyde could be detected in green leaves which had been exposed to the light, but not in those exposed to the dark, but this fact does not necessarily imply that the Baeyer hypothesis as to the formation of formaldehyde from carbon dioxide is correct, as the aldehyde can be the product of photochemical decomposition of other products. The results indicate that the existence of a deaminase is not proven.
S. B. S.

The Protein Content of Variegated Leaves Investigated by Molisch's Macroscopic Method. GEORG LAKON (*Biochem. Zeitsch.*, 1916, **78**, 145—154).—According to Molisch, the presence of proteins can be demonstrated in leaves which have been treated with hot water and then alcohol by means of the biuret, xanthoproteic, and Millon reagents. This method has been applied by the author with many leaves, especially the variegated leaves of *Acer negundo*. The green parts give marked protein reactions,

whereas the white parts remain almost uncoloured. The chromatophores appear to contain, therefore, the greatest amounts of protein. In this respect, Molisch's conclusions are confirmed.

S. B. S.

Proteins of the Peanut, *Arachis hypogaea*. II. Distribution of the Basic Nitrogen in the Globulins Arachin and Conarachin. CARL O. JOHNS and D. BREESE JONES (*J. Biol. Chem.*, 1917, **30**, 33—38. Compare this vol., i, 191).—The globulins of the peanut contain the basic amino-acids, arginine, histidine and lysine and cysteine. Arachin contains 5% and conarachin 6% of lysine. The relatively high percentage of lysine in the proteins of the peanut suggests that this seed might be used to advantage in supplementing diets deficient in lysine.

H. W. B.

Substance accompanying Lapachol in Greenheart Wood. O. A. OESTERLE (*Arch. Pharm.*, 1916, **254**, 346—348).—The author has isolated from the greenheart wood of *Bignonia leucoxydon*, in addition to lapachol, a very small quantity of a substance, $C_{23}H_{26}O_4$, colourless needles, m. p. 222—223°, darkening at 215°, which is not volatile with steam, is insoluble in alkali hydroxides or carbonates, and develops a bluish-violet coloration with concentrated sulphuric acid. It is certainly not lapachonone, which not infrequently accompanies lapachol in woods. C. S.

Microchemistry of Plants. IV. Organic Lime-balls and Siliceous Bodies in Capparis. HANS MOLISCH (*Ber., Deut. bot. Ges.*, 1916, **34**, 154—160).—Almost every parenchymatous cell of the leaf-stem of *Capparis callosa* contains a spherical, colourless, highly refractive body, which is found to be an organic calcium compound, possibly a double malate of calcium and magnesium. Bodies containing silicic acid and an organic substance are also present. These two bodies are also found in the leaf itself and in the stem of the plant.

T. H. P.

Plant Food Materials in the Leaves of Forest Trees. PAUL SEREX, jun. (*J. Amer. Chem. Soc.*, 1917, **39**, 1286—1296).—The leaves of the chestnut (*Castanea Dentata*), the sugar maple (*Acer saccharum*), and white oak (*Quercus alba*) were gathered in spring and autumn from apparently healthy specimens on different types of soil, and were examined as to their content of phosphorus, potassium, and nitrogen. The spring leaves contained a higher proportion of nitrogen and potassium than the autumn leaves from the same trees, whilst the percentage of phosphorus varied with the species and the section of the tree from which the leaves were obtained. The content of nitrogen, phosphorus, and potassium was higher in leaves from trees on a loam soil than from those on clay soil; with the maple and oak the percentage of these elements was generally higher in leaves from the upper branches, whereas with the chestnut the reverse appeared to be the case.

D. F. T.

Anatomy and Chemism of the Lichen, *Chrysothrix nolitangere*. EMANUEL SENFT (*Ber. Deut. bot. Ges.*, 1916, 34, 592—600).—This lichen seems to owe its yellow colour only to the calycin present.
T. H. P.

Raffinose in the Seed of the Jute Plant (*Corchorus capsularis*). HAROLD EDWARD ANNETT (*Biochem. J.*, 1917, 11, 1—6).—The seeds of the jute plant contain between 2% and 3% of raffinose.
H. W. B.

Microchemistry of Droseraceæ. M. FÜNFSTÜCK and R. BRAUN (*Ber. Deut. bot. Ges.*, 1916, 34, 160—168).—The root and leaf-stems of *Drosera binata* contain numerous crystalline needles which closely resemble, but are not identical with, the crystalline tannin found by Molisch in *Dionaea muscipula* (*A.*, 1916, i, 195). The latter is now found to contain both these compounds.
T. H. P.

The Proteoclastic Enzymes of *Drosera rotundifolia*. K. G. DERNBY (*Biochem. Zeitsch.*, 1916, 78, 197—199).—The preparation used was a dialysed glycerol extract of the leaves. This contains a pepsin-like enzyme, but no trypsin or erepsin.
S. B. S.

Microchemistry of Plants. II. Orange-coloured Hydathodes in *Ficus javanica*. III. Brown Colouring Matter of "Golden-yellow" Grapes. HANS MOLISCH (*Ber. Deut. bot. Ges.*, 1916, 34, 66—72).—Orange-yellow points occurring on the upper side of leaves of *Ficus javanica* are found to be due to numerous rounded or irregular bodies containing carotin.

The pale or dark brown ("goldgelbe") colour of that side of ripe green grapes which is exposed to the light is found to be due to the conversion of tannin into phlobaphen as a result of prolonged illumination.
T. H. P.

Microchemistry of Plants. VIII. Readily Crystallisable Organic Substance in *Linaria* Species. HANS MOLISCH (*Ber. Deut. bot. Ges.*, 1917, 35, 99—104).—The epidermis of *Linaria genistifolia* and of certain other species (*L. bipartita* and *L. reticulata*) contains an almost saturated solution of an organic substance which, shortly after the epidermis is placed in a drop of water on a microscope slide, crystallises out in single or twinned spherites, double brush forms, or prisms of a pale yellow colour. Treatment of the epidermis with alcohol, glycerol, acetone, ether, chloroform, sugar solution, xylene, 10% hydrochloric, nitric, or sulphuric acid, 5% oxalic acid solution, or concentrated acetic acid causes immediate precipitation of the substance. Sodium carbonate solution (10% or saturated) or 10% potassium carbonate solution colours the crystals an intense yellow, but does not dissolve them, whilst potassium, sodium, or barium hydroxide solution or ammonia solution dissolves them, giving yellow solutions. The substance occurs in the epidermis of all parts of the plant with the exception of the root.
T. H. P.

Occurrence of ψ -Cubebin in *Ocotea usambarensis*, Engl. JOSEF HALBERKANN (*Arch. Pharm.*, 1916, 254, 246—255).—The author has isolated from the bark of *Ocotea usambarensis*, Engl. (Ibean camphor tree), a substance, $C_{20}H_{30}O_6$, needles, m. p. 121.5—122°, $[\alpha]_D^{25} + 60$ —61° in chloroform, which appears to be identical with Peinemann's ψ -cubebin. C. S.

Microchemistry of Plants. VII. Serratulin. HANS MOLISCH (*Ber. Deut. bot. Ges.*, 1916, 34, 554—559).—The statement occurring in the literature to the effect that *Serratula tinctoria* contains in vivo a yellow colouring matter is erroneous. The cells of the living plant contain a colourless or almost colourless substance, serratulan, which undergoes post-mortem transformation, under the influence of various materials, into an intensely yellow substance, serratulin. Serratulan occurs in the root and stem, and in particular abundance in the leaves. T. H. P.

Action of Illuminating Gas on Plants. I. Action of the Gas on the Germination of Spores and Seeds. C. WEHMER (*Ber. Deut. bot. Ges.*, 1917, 35, 135—154).—The results of experiments made show that illuminating gas exhibits no general poisonous character towards plants. Anaerobic fungi grow even in the undiluted gas, and cress seeds (*Lepidium sativum*) remain alive in it for weeks. It retards the growth of the embryo, but this proceeds uninterruptedly if the gas is diluted with about five times its volume of air. Gas is thus not an acute plant poison, but if it is passed for some time through soil, the latter becomes incapable of permitting seeds to germinate and grow in it; after such soil has been extracted with cold water, it behaves normally towards seeds, the injurious properties being transferred to the water. The principal constituents of coal-gas to which its action on plants is due are sulphur compounds, benzene and its homologues, and, to a less extent, ethylene. Carbon monoxide is without effect on plants. T. H. P.

Physical Chemistry of Foods. III. The Chemical Equilibrium between Tartaric Acid and Potassium Tartrate as Basis of the Reduction of the Acidity of Wine by means of this Salt. THEODOR PAUL (*Zeitsch. Elektrochem.*, 1917, 23, 65—87. Compare A., 1915, ii, 590; this vol., i, 246).—Since the degree of acidity of a wine is identical with its hydrogen ion concentration, and the strength of the acid taste is directly proportional to this, it follows that the deacidification of wine by means of normal potassium tartrate brings about a reduction of the hydrogen ion concentration. The chemical equilibrium between tartaric acid and its potassium salt therefore plays an important part in the deacidification of wine by means of this salt. This equilibrium has been studied in the present paper, and the equations which express the equilibrium have been experimentally substantiated. A litre of pure, carbon dioxide-free water at 18° dissolves 4.903 grams = 0.02606 gram-mol. of potass-

ium hydrogen tartrate; the solubility product of this salt, $[K^+][HC_4H_4O_6^-]$, in water at 18° is equal to 3.8×10^{-4} , in aqueous alcohol (8% alcohol) 1.3×10^{-4} . The addition of ethyl alcohol, amounting to 80 grams per litre, therefore exerts a marked influence on the chemical equilibrium; further, the ionisation constant of tartaric acid in such a mixture is considerably less than in pure water. During the gradual deacidification of an aqueous solution of tartaric acid by means of normal potassium tartrate, the decrease in the acidity is much greater at the commencement than later. The titratable acid remains constant until the precipitation of potassium hydrogen tartrate commences, and then decreases in proportion to the amount of normal potassium tartrate added and the amount of potassium hydrogen tartrate precipitated. The values of the individual concentrations, both of ions and molecules during the deacidification of 10% aqueous or aqueous alcohol solutions of tartaric acid can be calculated by means of the equation put forward, and also the electrical conductivity of the equilibrium solutions can be calculated by the same means, giving values which agree well with the experimentally determined figures. When the deacidification process is carried out with natural wine, the same phenomena are, in general, observed as in the case of aqueous and aqueous-alcoholic solutions of tartaric acid. At the commencement, however, the decrease in the acidity is not so marked as with these solutions. This is due, in the first place, to the earlier precipitation of potassium hydrogen tartrate, since the wine usually contains a considerable amount of this salt. Further, the wine also contains considerable quantities of still weaker acids than tartaric acid. The deacidification of wine in this manner does not follow the simple equation $K_2C_4H_4O_6 + H_2C_2H_4O_6 = 2HKC_4H_4O_6$, as was previously believed, but is a much more complicated process. The following advantages are claimed for this method of deacidifying wine: (1) It introduces no foreign substance into the wine, since both potassium and tartaric acid are already there. (2) The greater part of the added substance is precipitated as potassium hydrogen tartrate, so that the ash and extract of the wine are not greatly increased. (3) This treatment does not so seriously change the constitution of the wine as does the deacidification with chalk. (4) Since normal potassium tartrate can be added to wine as a concentrated aqueous solution, which is impossible when chalk is used, the process is a homogeneous one from the beginning, and equilibrium is set up much more rapidly. Consequently, it is not necessary to keep the wine for long periods after deacidification; in general, it is found that the precipitation of potassium hydrogen tartrate is complete in twenty-four hours. This treatment does not produce a turbidity in the wine. (5) Since the degree of acidity of the wine remains the same, whether the solution is supersaturated with potassium hydrogen tartrate or not, the deacidification can be effected by simply running a solution of normal potassium tartrate into it until a sample possesses the correct taste.

J. F. S.

Physical Chemistry of Foods. IV. Scientific Wine Tests to Determine the Relationship between the Strength of the Acid Taste and the Hydrogen Ion Concentration. THEODOR PAUL (*Zeitsch. Elektrochem.*, 1917, 23, 87—93. See preceding abstract).—An account of a number of experiments undertaken to show that it is possible to differentiate between and place in order a series of wines of different acidities. Moselle wine containing hydrogen ion of the concentrations 1·8, 0·95, 0·55, and 0·25 mg. ion per litre was submitted to sixty-four people. Of these, thirty-seven by taste alone correctly placed the four samples, eighteen people misplaced one sample, and to one person they all tasted alike.
J. F. S.

An Artificial Soil, almost free from all Mineral or Organic Matter, suitable for the Study of Plant Cultures and for the Examination of the Influence of Different Fertilisers. A. GAUTIER (*Compt. rend.*, 1917, 164, 985—986).—The medium is prepared by heating finely powdered coal to a red heat, boiling the product with acid, and finally washing it with distilled water.
W. G.

Action of Various Salt Solutions on the Permeability of the Soil. D. J. HISSINK (*Bied. Zentr.*, 1917, 46, 138—140).—Experiments with water and solutions of sodium, potassium, ammonium, and calcium chlorides indicate that the action of salt solutions on the permeability of the soil is not solely physical in character, but is probably dependent principally on chemical processes.
T. H. P.

Relation of the Water-retaining Capacity of a Soil to its Hygroscopic Coefficient. FREDERICK J. ALWAY and GUY R. MCDOLE (*J. Agric. Research*, 1917, 9, 27—71).—A description of various experiments with uniform columns of soil of known hygroscopic coefficient and moisture equivalent to determine the distribution of water in the soil under different conditions. The soils used varied in texture from a coarse sand to a silt loam, having hygroscopic coefficients of 0·6 and 13·3 respectively.

Five such loams, placed in capillary connexion with a subsoil, were saturated with water from the top and allowed to remain protected from surface evaporation for several months. They lost water until the amount retained was from 2·1 to 3·1 times the hygroscopic coefficient of the particular soil. If a layer of coarse sand or gravel was interposed between the column of loam and the subsoil, the downward movement of the water in the loam was materially checked. Using a column made up of successive 5 cm. layers of loams differing in texture, the final water-content was independent of the order of their arrangement.

Using soil columns 75 to 85 cm. long, protected from all loss of moisture from the sides and bottom, but freely exposed to evaporation for times varying from three weeks to half a year, the moisture-content, originally uniform, fell until it reached, at depths below 30 cm., an almost constant minimum of 1·9 to 2·2 times the hygroscopic coefficient.

A comparison was made of twelve different loams, using 60 cm. columns and applying water in one series at the base and in the other at the top, in quantity sufficient to bring the average moisture-content of the columns up to 1.5 times their hygroscopic coefficient. The columns were protected at all surfaces from evaporation, and after four months the distribution of moisture with reference to the surface of application was found to be the same in each series. The maximum final ratio of moisture-content to hygroscopic coefficient was found in all cases in the 7.5 cm. adjacent to the surface of application, where it lay between 1.7 and 2.4. This ratio is not the same for all soils having the same hygroscopic coefficient. From these laboratory experiments the water-retaining capacity of the loams appears to bear a closer relationship to the moisture equivalent than to the hygroscopic coefficient.

Coarse sands behave very differently from loams. Three months after the application of 2.5 cm. of water, the surface 15 cm. section had a ratio of 6.0—7.0, whilst in the second 30 cm. it was only 1.0. These results were confirmed by field studies. Fine sands apparently occupy an intermediate position between the coarse sands and the loams.

Field studies show that loams, if thoroughly moistened with rain and protected from losses by evaporation and transpiration, lose water by downward movement until the ratio of moisture-content to hygroscopic coefficient lies between 1.8 and 2.5, and this is the ratio which may be expected in the subsoil, below the range of plant roots, in dry-land regions.

In cases where the subsoil has been previously exhausted of available water to a considerable depth by plants, it is found, even several months after heavy rain, that there is an abrupt transition from the moistened soil to the exhausted subsoil, the ratio dropping from 2.2 to 1.0. The moisture of the deeper subsoil will be able to move upward only so slowly and through such a short distance in a year as to be of no practical benefit to annual crops. In order to make use of it, deep-rooting perennials must be grown at intervals.

W. G.

Measurement of the Inactive, or Unfree, Moisture in the Soil by means of the Dilatometer Method. GEORGE J. BOUYOUCOS (*J. Agric. Research*, 1917, 8, 195—217).—A dilatometer is described in which determinations have been made of the amount of water in soils failing to freeze when super-cooled to -3° . Various types of soil were examined, varying from a quartz sand to a heavy, black clay, and in each case the sample was prepared by adding 5 c.c. of water to 25 grams of air-dry soil. The bulb of the dilatometer was kept in a freezing mixture at -4° , and when the temperature inside the bulb was -3° the dilatometer was gently shaken until solidification began, and the expansion was read when equilibrium was reached. Under these conditions it was found that the amount of water failing to freeze varied from 2% in quartz sand to 80% in clay, of the water added. The more colloidal the character of the soil, the lower was the amount of water which

froze. The values obtained by this method correspond closely with the moisture contents known as the wilting coefficient, with the percentage of moisture at which solidification cannot be started and with the thermal critical moisture coefficient. This water which fails to freeze is designated as unfree or inactive water, and the evidence indicates that a large portion of it may exist as physically adsorbed and loosely chemically combined, the quantity of the latter probably exceeding that of the former. This inactive water is not in a stable condition, since the amount can be caused to vary by different modes of treatment. Thus in colloidal soils, increasing the super-cooling causes it to diminish, and a similar effect is obtained by increasing the degree of moisture content of the soil. Successive freezings also diminish the amount of water failing to freeze in colloidal soils.

W. G.

Fixation of Ammonia in Soils. I. G. McBETH (*J. Agric. Research*, 1917, 9, 141—155).—Many semi-arid subsoils have the property of fixing relatively large quantities of ammonia, a large percentage of the ammonia added in the form of ammonium salts not being recovered by the ordinary methods for determining the ammonia-content of soils. This fixation is not influenced by the anion of the ammonium salt. The ammonia added cannot be recovered by boiling the soil with excessive amounts of potassium or sodium hydroxide. Boiling with 10% hydrochloric acid in one case removed practically all the ammoniacal nitrogen and in another case 75% of it. The fixation of ammonia by semi-arid soils increases with the depth in the soil, with the concentration of the solution of the ammonium salt, and with rise in temperature. With the addition of small amounts of ammonium salts, the percentage fixation remains constant, but if increasing amounts are added the percentage fixation diminishes, whilst the absolute fixation tends to rise to a maximum. The fixation is most rapid during the first few minutes, and then proceeds slowly for several days. Heating the soil at 200° or above for six hours considerably reduces its power of fixing ammonia.

Aluminium, iron, and potassium salts added to soils prior to the addition of ammonia decidedly reduce the ammonia-fixing power of the soils, whilst calcium, magnesium, and sodium salts have but little effect on the ammonia-fixing power of these soils. The anions of these metallic salts do not exert any influence on these phenomena. In semi-arid soils the quantity of calcium brought into solution by ammonium chloride increases with the depth. When extracted with aluminium, sodium, or magnesium chloride, the calcium brought into solution does not increase with the depth.

W. G.

Availability of Potash in certain Orthoclase-bearing Soils affected by Lime or Gypsum. LYMAN J. BRIGGS and J. F. BREAZEALE (*J. Agric. Research*, 1917, 8, 21—28).—Experiments with pegmatite and orthoclase show that the solubility of their potassium in water is not affected by the presence of calcium hydr-

oxide. The presence of calcium sulphate tends to diminish the solubility of the potassium in the orthoclase, the solubility decreasing as the concentration of the calcium sulphate increases. Similar results were obtained with a virgin soil of granitic type, and these were confirmed by determining the potassium content of wheat seedlings grown on (a) water containing finely ground orthoclase, (b) the same saturated with calcium sulphate. W. G.

Transformation of the Sesquioxides in Woodland Soils. (Formation of Ortstein and Laterite.) H. STREMMER (*Kolloid Zeitsch.*, 1917, 20, 161—168).—The theory that ferric oxide and alumina in the soil are the result of the coagulation of corresponding sols, is examined in reference to the influence of the chemical and physical characters of the soil, climate, and vegetation. The composition of the soil solution, and in particular the amount of soluble organic substance present, is of primary importance in connexion with the coagulation process. H. M. D.

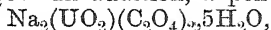
The Organic Matter of the Soil. V. The Nitrogen Distribution in different Soil Types. CLARENCE AUSTIN MORROW and ROSS AIKEN GORTNER (*Soil Sci.*, 1917, 3, 297—331).—Three grams of fibrin were subjected to protein analysis by the Van Slyke method, the initial hydrolysis being carried out in presence of 100 grams of ignited subsoil. The figures thus obtained were compared with those of a similar analysis carried out without the presence of the soil, and it was found that the two sets of figures were in excellent agreement except for the fact that whereas the fibrin hydrolysed alone yielded 4.36% of its nitrogen in the histidine fraction and 2.83% as 'humin,' the fibrin hydrolysed with the subsoil yielded no histidine nitrogen and 7.59% of 'humin.' Although it appeared likely that the presence of soil had caused the histidine nitrogen to be converted into 'humin' nitrogen, pure histidine dihydrochloride underwent no such conversion when boiled with hydrochloric acid for forty-eight hours in presence of subsoil. The Van Slyke method of protein analysis was then applied to a series of soils of various types, and the authors point out that although the data obtained for the different fractions may not be comparable to similar data obtained from pure proteins, they are of value for comparing the distribution of the nitrogen amongst the different fractions in various soil types. The results of the analyses showed that when expressed as a percentage of the total nitrogen in the soil, the nitrogen dissolved by the acid hydrolysis was practically constant, irrespective of the nature or the condition of the soil under investigation. The same is true of all the other fractions isolated, and the conclusion may be drawn that the organic compounds of nitrogen in different soil types are very uniform.

As a result of their investigations, the authors suggest the advisability of estimating a further fraction in connexion with the 'humin' nitrogen. L. M. U.

Organic Chemistry.

The System Water-Uranyl Oxalate-Sodium Oxalate.

A. COLANI (*Compt. rend.*, 1917, 165, 111—113).—An examination of the solubility curves of the system water-uranyl oxalate-sodium oxalate at 15° and 50° shows the existence of two new compounds having the composition $\text{Na}_3(\text{UO}_2)_4(\text{C}_2\text{O}_4)_5, 11\text{H}_2\text{O}$ and $\text{Na}_2(\text{UO}_2)_2(\text{C}_2\text{O}_4)_3, 5\text{H}_2\text{O}$. In addition, a pentahydrate,



was obtained, the crystals of which were macroscopically identical with those of the hexahydrate described by Wyruboff (compare *Bull. Soc. franc. Min.*, 1909, 32, 351, 357, 364). No indication of the salt $\text{Na}_6(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5, 13\text{H}_2\text{O}$ described by Wyruboff (*loc. cit.*) could be obtained. At 75°, from a solution containing 1.5 mols. of sodium oxalate to 1 mol. of uranyl oxalate, crystals were deposited having the composition $\text{Na}_{10}(\text{UO}_2)_4(\text{C}_2\text{O}_4)_9, 12\text{H}_2\text{O}$.

W. G.

Isomerisation and Hydration of Citronellaldehyde by

Acids. H. J. PRINS (*Chem. Weekblad*, 1917, 14, 627—630).—Formic acid (85—90%) or phosphoric acid (80%) converts citronellaldehyde into an oil which, on distillation in a vacuum, yields 10% of isopulegol; 15—20% of a condensation product of 2 molecules of citronellaldehyde, b. p. 185°/13 mm.; isopulegol hydrate, acicular crystals, m. p. 84—85°; and a heptacyclic glycol, $\text{C}_{10}\text{H}_{20}\text{O}_2$, m. p. 60—62°.

A. J. W.

Action of Acids on the Rotatory Power of Sucrose and Invert-sugar in the Presence of Soluble Salts.

EM. SAILLARD (*Compt. rend.*, 1917, 165, 116—118).—[With WEHRUNG.]—Sulphurous and acetic acids, at the concentrations used, have no effect on the rotatory power of sucrose in the presence of sodium chloride, but they diminish that of invert-sugar in the presence of this salt, to which they are thus antagonistic. Hydrochloric acid increases the levorotatory power of invert-sugar in the presence of sodium chloride. Carbon dioxide is without action on the rotatory power of either sucrose or invert-sugar in the presence of sodium chloride.

W. G.

The Chemistry of Caramel. I. Caramelan.

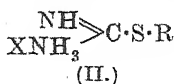
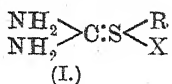
MARY CUNNINGHAM and CHARLES DORÉE (*T.*, 1917, 111, 589—608).—Believing that a study of the process of the formation of caramel may have a bearing on the problem of the constitution of cellulose and the question of the production of humus, peat, and coal, the authors have begun a systematic investigation by a contribution on the nature of caramelan.

When sucrose is heated at 170—180° until the loss of weight is

12%, it loses two molecules of water, some furfuraldehyde, pungent acid vapours, and carbon dioxide being evolved as well, and leaves practically pure caramelan, $C_{12}H_{18}O_9$, or probably $C_{24}H_{36}O_{18}$, m. p. 136°. This yields a tetra-acetate, m. p. 107°, a *tetrabenzoate*, m. p. 105—108°, and an explosive *tetranitrate*. It behaves like a ketose in forming precipitates with resorcinol and phloroglucinol, and it also condenses with phenylhydrazine and semicarbazide, but the products are not simple hydrazones or semicarbazones, but derivatives of a $C_{24}H_{36}O_{18}$ molecule less several molecules of water. When shaken with 40% hydrochloric acid, caramelan is not hydrolysed as is cellulose, or hydrolysed and then converted partly into ω -chloromethylfurfuraldehyde like sucrose, but is dehydrated further to caramelin, $C_{24}H_{26}O_{13}$. Dilute sulphuric and hydrochloric acids, however, cause hydrolysis and dehydration at the same time, dextrose, methylfurfuraldehyde, furfuraldehyde, humic acid, $C_{24}H_{22}O_{11}$, and a chlorinated humic acid, $C_{24}H_{20}O_{18}Cl_3$, having been found among the products.

The action of various oxidising agents on caramelan has also been investigated. The products are very complex, but are mostly derivatives of a C_{23} unit. Acetaldehyde was obtained from the ozonide, indicating that a $CHMe:C$ residue is present in caramelan, whilst dilute nitric acid yielded an insoluble, red, nitrated humic acid, $C_{23}H_{23}O_{13} \cdot NO_2$, and a soluble, ketonic nitro-acid, $C_{17}H_{15}O_{10}N$.
J. C. W.

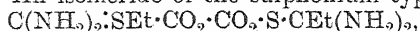
Constitution of the Salts of S-Alkylthiocarbamides. JOHN TAYLOR (T., 1917, 111, 650—663).—Additive compounds of thiocarbamide with alkyl haloids have been known for a long time. Similar compounds with methyl, benzyl, and ethyl sulphates, nitrates, and thiocyanates have now been obtained, the readiness with which combination takes place falling off in the order in which the radicles are named, which is the same as in the case of the haloids. These compounds all behave like salts, in which the acidic ions respond to the usual tests. From one salt another can be made by double decomposition, so that it is possible to prepare salicylates, acetates, and phosphates, which cannot be obtained directly. Two formulæ only need therefore be considered in connexion with the constitution of these additive compounds, namely, the "sulphonium" (I) and "ammonium" (II):



Since the compounds with benzyl nitrite and methyl and benzyl thiocyanates are stable in boiling water, the ammonium type is improbable, but in the case of benzyl esters of strong acids, two isomerides are met with, and one of them is then of this type. The conditions for the formation of the ammonium salts are that the free mineral acids shall be present during the crystallisation of the salt, and the sulphonium salts can be obtained from them

by boiling with water alone or with a very dilute aqueous or alcoholic solution of sodium phosphate. Salts prepared by double decomposition are always of the sulphonium type, even if an "ammonium" salt is used.

Nencki (1874) described an additive compound of thiocarbamide with ethyl oxalate which has m. p. 158° , does not give a precipitate of calcium oxalate until hydrolysed, and yields a metallic sulphide when warmed with alkaline lead solutions or ammoniacal silver nitrate. An isomeride of the sulphonium type,



is obtained if the compound of thiocarbamide with ethyl iodide is treated with silver oxalate. This has m. p. 188° , gives a precipitate of calcium oxalate at once, and produces metallic mercaptides and cyanamides with the above lead or silver solutions.

When thiocarbamide oxalate is warmed with alcohol, Nencki's compound is formed. This is explained by assuming that oxalic acid is given up by the thiocarbamide salt, that ethyl oxalate is then formed, and that this ester combines with the free thiocarbamide. Such evidence was required when a similar explanation of the action of acetaldehyde on thiocarbamide hydrochloride was advanced (Dixon and Taylor, this vol., i, 11).

For the details of the numerous salts, many of which had been described by Arndt as salts of alkyl- ψ -thiocarbamides (A., 1911, i, 918), the original should be consulted. J. C. W.

Diazomethane. F. H. LORING (*Chem. News*, 1917, 115, 255).—An ethereal solution of diazomethane is obtained by distilling from a retort in a water-bath a mixture of 2.5 c.c. of nitrosomethylurethane, 25 c.c. of dry ether, and 1.75 c.c. of methylalcoholic potassium hydroxide (1:4), and collecting the distillate in a freezing mixture of ice and calcium chloride. G. F. M.

Preparation of Benzenesulphonic Acid. COMP. DES PRODUITS CHIMIQUES D'ALAIS and DE LA CAMARGUE (Brit. Pat., 101973, 1916; from *J. Soc. Chem. Ind.*, 1917, 36, 705).—Benzenesulphonic acid is prepared by passing benzene vapour into sulphuric acid of any concentration, preferably at 120 – 130° . Water is eliminated as steam, and the sulphonic acid crystallises on cooling. D. F. T.

Method of Separating Benzenedisulphonic Acid from Sulphuric Acid and Converting it into a Salt. L. M. DENNIS (U.S. Pat., 1227252, 1917; from *J. Soc. Chem. Ind.*, 1917, 36, 705).—The mixture of disulphonic acid and sulphuric acid is extracted with an organic solvent, for example, benzene, and the resulting solution is treated with a suitable compound to convert the dissolved disulphonic acid into a salt. D. F. T.

The Alcohols and Bases of Vacuum Tar. AMÉ PICTET, O. KAISER, and A. LABOUCÈRE (*Compt. rend.*, 1917, 165, 113–116).—The authors have isolated from vacuum tar 4-methylcyclohexanol, and the alcohols from C_8 to C_{11} , inclusive, of the

homologous series $C_nH_{2n-6}O$. The last four alcohols are unsaturated, and are spontaneously and fairly rapidly converted into phenols, this process being accelerated by heat. Their acetates, which are colourless, volatile liquids, instantly decolorise potassium permanganate in cold sulphuric acid solution. The bases isolated consist of a product, C_7H_9N , and the members from C_3 to C_{12} , inclusive, of the homologous series $C_nH_{2n-9}N$. The first-named base is probably a mixture of toluidines. The other bases are unsaturated, secondary amines, with odours resembling those of quinoline and its homologues. The physical properties of the alcohols and their acetates, and the bases and their picrates, are as follows:

Alcohols.			Bases.		
Formula	B. p.	Acetate. B. p.	Formula.	B. p.	Picrate. M. p.
$C_7H_{14}O$...	170—175°		C_7H_9N	198—203°	170°
$C_8H_{16}O$...	185—190		C_8H_9N	225	195
$C_9H_{18}O$...	198—200	213—215°	C_9H_9N	247—250	184
$C_{10}H_{20}O$...	213—215	226—229	$C_{10}H_{11}N$	250—260	184
$C_{11}H_{22}O$...	226—228	240—244	$C_{11}H_{13}N$	260—265	173
			$C_{12}H_{15}N$	270—280	166

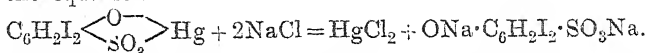
W. G.

Soziodol-Mercury Compounds. E. RUPP and A. HERRMANN (*Arch. Pharm.*, 1916, **254**, 488—497).—Pharmaceutical preparations containing organic mercury compounds belong to two classes, namely, those containing ionisable mercury, for example, hydrargyrum benzoicum, and those, such as hydrargyrum salicylicum, containing nuclear, non-ionisable mercury. Some such preparations, which are insoluble in water, dissolve readily in a solution of sodium chloride. This solubility is due, in the case of substances of the former class, to ordinary double decomposition with formation of mercuric chloride, and in the case of substances of the latter class to the formation of the sodium salts of chloromercuri-aromatic acids by the addition of sodium chloride.

Soziodol-mercury ($C_6H_2I_2\langle\begin{smallmatrix} O \\ SO_3 \end{smallmatrix}\rangle Hg$) belongs to neither of the preceding classes, and therefore the cause of its solubility in a solution of sodium chloride or potassium iodide has been investigated, and also the explanation of its orange colour. The substance has been prepared in several different ways: (1) by the reaction in hot aqueous solution between mercuric nitrate and an equivalent amount or an excess of sodium soziodolate (2:6-di-iodophenol-*p*-sulphonate); (2) from yellow mercuric oxide and an equivalent quantity or an excess of soziodolic acid in aqueous solution; and (3) by adding a warm aqueous solution of sodium soziodolate to the equivalent amount of a mercuric acetate solution. If in the last method the order of the addition is reversed and the solutions are at the ordinary temperature, a red substance, $(SO_3Na \cdot C_6H_2I_2 \cdot O)_2Hg$, is at first precipitated, which is converted into soziodol-mercury by the addition of more mercuric acetate

solution. This red substance is better obtained by digesting yellow mercuric oxide and sodium sozoiodolate (2 mols.) in lukewarm water; it dissolves in aqueous sodium chloride, forming a colourless solution.

When a solution of sozoiodol-mercury in aqueous sodium chloride is extracted with ether, the extract is found to contain mercuric chloride in nearly the theoretical amount corresponding with the equation



The disodium sozoiodolate is difficult to isolate on account of its great solubility, but when a concentrated solution of sozoiodol-mercury in aqueous sodium chloride is acidified, sodium sozoiodolate is precipitated in slender needles containing $2\text{H}_2\text{O}$. The disodium salt forms large, rectangular crystals containing $5\text{H}_2\text{O}$, having a faintly alkaline reaction. The dipotassium salt is formed, together with potassium mercuric iodide, when sozoiodol-mercury dissolves in aqueous potassium iodide; by adding the latter very carefully, mercuric iodide is obtained in quantitative amount.

The brick-red substance, $\text{C}_6\text{H}_2\text{I}_2 \left\langle \begin{array}{c} \text{O}-\text{Hg}-\text{O} \\ \text{SO}_3 \cdot \text{Zn} \cdot \text{SO}_3 \end{array} \right\rangle \text{C}_6\text{H}_2\text{I}_2$, is obtained by digesting mercuric oxide and zinc sozoiodolate with warm water; it resembles the corresponding sodium salt in its behaviour. These two substances are coloured, and so also is *mercuric 2:4:6-tribromophenoxide*, $(\text{C}_6\text{H}_2\text{Br}_3 \cdot \text{O})_2\text{Hg}$, yellowish-red crystals, prepared from mercuric acetate and tribromophenol in aqueous-alcoholic solution; it appears, therefore, that the group $\cdot\text{O} \cdot \text{Hg} \cdot \text{O} \cdot$ exerts a chromophoric function, and thus the colour of sozoiodol-mercury is accounted for.

Potassium 2:6-di-iodophenetole-p-sulphonate, $\text{OEt} \cdot \text{C}_6\text{H}_2\text{I}_2 \cdot \text{SO}_3\text{K}$, colourless needles, is prepared by heating potassium sozoiodolate (1 mol.) and potassium hydroxide (1.1 mols.) dissolved in a little water with an alcoholic solution of ethyl iodide (1.1 mols.) at about 130° . The corresponding *barium* salt, needles with $5\text{H}_2\text{O}$, and *mercuric* salt, colourless needles, have been prepared; *2:6-di-iodophenetole-p-sulphonic acid* forms crystals with $2\text{H}_2\text{O}$, m. p. 108° .

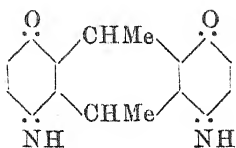
The constitution of sozoiodolic (2:6-di-iodophenol-*p*-sulphonic) acid is proved by the facts that the acid (1) yields 2:4:6-tri-iodophenol, iodine, and phenol by heating with fuming hydrochloric acid at about 120° , and (2) is formed by treating 2:6-dihydroxy-mercuriphenol-*p*-sulphonic acid (Rupp and Herrmann, this vol., i, 488) with a solution of iodine.

Anogon ($\text{OHg} \cdot \text{C}_6\text{H}_2\text{I}_2 \cdot \text{SO}_3\text{Hg}$) does not form a clear solution in aqueous sodium chloride, a precipitate of mercurous chloride being produced.

C. S.

Action of Acetaldehyde-ammonia on Quinones. PRAPHULLA CHANDRA GHOSH (T., 1917, 111, 608—612).—*p*-Benzoquinone condenses with acetaldehyde-ammonia to form a black

compound, probably



hydrazone, $C_{18}H_{12}(:N\cdot NPh)_2$.

of the annexed formula, which reacts with cold nitric acid (D 1.45) to form a yellow compound, $C_{16}H_{12}O_6N_4$. These do not melt at 290° . Anthraquinone and acetaldehyde-ammonia react at 220° to yield a colourless, silky compound, m. p. 281° , to which the formula $C_6H_4 \langle \begin{smallmatrix} C(:CH\cdot CHO) \\ C(:CH\cdot CHO) \end{smallmatrix} \rangle C_6H_4$ is assigned, since it forms a yellow phenylhydrazone, $C_{18}H_{12}(:N\cdot NPh)_2$. J. C. W.

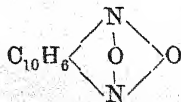
A Simple Demonstration of the Addition of Water to Terpeneol under the Influence of Acids. H. J. PRINS (*Chem. Weekblad*, 1917, **14**, 630—631).—When terpeneol is agitated with 80% phosphoric acid at 30° , it dissolves, and crystals of terpin hydrate separate. A less complete transformation is caused by 60% sulphuric acid, but 85% formic acid does not react.

A. J. W.

The Bromo-derivatives of Aloe-emodin. E. LÉGER (*J. Pharm. Chim.*, 1917, [vii], **16**, 5—8).—When aloe-emodin is heated in a sealed tube at 115° for eighteen hours with bromine, *pentabromoaloe-emodin*, $C_{15}H_5O_5Br_5$, slender, prismatic needles, m. p. 278.4° (corr.), is obtained. This compound is only very slowly soluble in cold dilute alkali hydroxide, but it dissolves at once on warming, and is converted into *tetrabromoaloe-emodin*, orange-red needles, m. p. 276.4° (corr.). W. G.

Equilibrium in the System: Cupric Chloride-Pyridine. J. HOWARD MATTHEWS and SAMUEL SPERO (*J. Physical Chem.*, 1917, **21**, 402—406).—Measurements of the solubility of cupric chloride in pyridine at temperatures between -17° and 95° show the existence of three compounds: $CuCl_2 \cdot 6C_5H_5N$, which is the stable solid phase up to -10° ; $CuCl_2 \cdot 2C_5H_5N$, stable between -10° and 58° ; and $2CuCl_2 \cdot 3C_5H_5N$, which is the stable phase above 58° . The first of the three compounds has not been previously described. H. M. D.

Conversion of *o*-Nitroamines into *iso*Oxadiazole Oxides, and of *o*-Nitrosoamines into *iso*Oxadiazoles. ARTHUR G. GREEN and FREDERICK MAURICE ROWE (T., 1917, **111**, 612—620).—In three earlier papers (T., 1912, **101**, 2452; 1913, **103**, 897, 2023), it was shown that many *o*-nitroamines are converted into *isooxadiazole* oxides (furoxans, furazan oxides) when oxidised by alkaline sodium hypochlorite. 2-Nitro-1-naphthylamine and 1-nitro-2-naphthylamine are no exceptions to this generalisation, for they both yield the same naphth*isooxadiazole* oxide or naphthafuroxan (annexed formula), m. p. 127° . This compound is the " β -naphthaquinone-dioxime peroxide" of Forster and Fierz (T., 1907, **91**, 1942) and also the "1:2-dinitroso-naphthalene" of Koreff and Ilinski. It yields β -naphthaquinonedioxime on reduction with



hydroxylamine, and this gives *naphthisooxadiazole* (*naphthafurazan*), $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} O$, m. p. 78° , on boiling with sodium hydroxide.

8-Nitro-1-naphthylamine does not yield a furoxan by this treatment, and 2:4-dinitronaphthylamine suffers rupture of the ring, which agrees with the authors' earlier experiences and interpretation of the mechanism of the reaction.

The oxidation of *o*-nitrosoamines by sodium hypochlorite is a similar reaction; the base passes through a quinonoid state to an *isooxadiazole* (fuzazan). Thus, 1-nitroso-2-naphthylamine and 2-nitroso-1-naphthylamine both yield the above *naphthisooxadiazole*. Similarly, *o*-nitrosoacetanilide (the free base could not be prepared) suffers hydrolysis and oxidation simultaneously, and gives *benzisooxadiazole* (benzfurazan). Crude *m*-nitrosoaceto-*p*-

toluidide likewise gives 5-methylbenzisooxadiazole, $C_6H_3Me \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} O$ (compare T., 1913, 103, 2023). J. C. W.

The Mechanism of the Ninhydrin Reaction. A Contribution to the Theory of Colour of Salts of Alloxantin-like Compounds. J. M. RETINGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1059—1066. Compare Ruhemann, T., 1911, **99**, 792, 1306). —A theoretical discussion of work published elsewhere (Diss., Leipzig, 1913) in which the author suggests the following course for the whole ninhydrin reaction. The triketohydrindene hydrate hydrolyses during boiling, giving *o*-carboxyglyoxal, which reduces part of the triketohydrindene to dioxindone, which then combines with another molecule of triketohydrindene to give hydrindantine. The amino-acid or amine derived from the enzyme action gives, first, as has been shown in the alloxantin series on alkali salts (*loc. cit.*), a monobasic salt which is colourless; further boiling produces a dibasic neutralisation, and the molecule then splits into two molecules with tervalent carbon, having a free valency, this being the cause of the absorption in the visible spectrum. The difference in colour at this stage is due to the different sizes of the molecules connected with the tervalent carbon, which results in a different potential for the free affinity of the carbon, and thus a different optical effect. Exposure to air in aqueous solution decomposes the split molecules further, giving *o*-carboxymandelic acid, ammonia, carbon dioxide, water, and an aldehyde. W. G.

Acid Hæmochromogen. CH. DHÉRÉ (*Compt. rend. Soc. de Biol.*, 1917, **79**, 1087—1090; from *Physiol. Abstr.*, 1917, **2**, 224). —A description of simple methods for preparing acid hæmochromogen by means of sodium hyposulphite. Acid hæmochromogen is more soluble in acetone than in methyl or ethyl alcohol. It is also soluble in ether, in methylal, in amyl alcohol, in benzene, and in toluene. It is not soluble in light petroleum,

and apparently not in glycerol. The solutions are stable for some months. G. B.

The "Mechanical Denaturation" of Proteins and the Method of Drying Organs for Biological Investigation. WILHELM WIECHOWSKI (*Biochem. Zeitsch.*, 1917, 81, 278—283).—The author confirms the observations of Herzfeld and Klinger (this vol., i, 300), according to which proteins dried on a plate become insoluble on scraping. For this reason, when organs are dried, the manipulation must be carried out in such a way that they can be dried into powder form and readily removed without such mechanical action from the material upon which they are spread. For this purpose, plates coated with solid paraffin can be used, and a preliminary account is given of a drying oven which can be employed, and which is designed to prevent the powder of the dried organs from being scattered by the current of air. S. B. S.

Physiological Chemistry.

The Differential Blood-gas Apparatus of Barcroft. E. MÜNZER and W. NEUMANN (*Biochem. Zeitsch.*, 1917, 81, 319—331).—An addition to Barcroft's apparatus is figured and described which has for its object its standardisation. This consists of a 1 c.c. pipette graduated in hundredths of a c.c., from which by means of a levelling tube a known volume of air can be driven into the manometer. The differences of level in the manometer corresponding with known volumes of air can thus be recorded when the standardisation is carried out at different atmospheric pressures and with different volumes in the pear-shaped vessels of the Barcroft apparatus. The constant k of the apparatus is obtained from the formula $v = kh$, where v is the volume of air driven in and h the difference in the heights of the olive oil in the two limbs of the manometer, and these are plotted for varying barometric heights and volumes of the pear-vessel. (In each case they are linear functions of these factors.) Attention is directed to an error in Barcroft's calculations, but it is pointed out that this does not materially affect his results. S. B. S.

The Presence of Phosphates in Human Blood-serum. I. The Phosphates Soluble in Acid in Normal and Pathological Sera. JOH. FEIGL (*Biochem. Zeitsch.*, 1917, 81, 380—425).—A general discussion of the question of the amount of phosphate in serum, with a criticism of the analytical methods and a summary of results obtained, supplemented by a large number of analyses by the author. In normal cases, the amount of "soluble"

phosphorus is less than 4 mg. per 100 c.c. (90% of the cases), but it is occasionally higher, and has been found to reach the amount of 10 mg. per 100 c.c. In certain pathological cases the amount is much higher.

S. B. S.

Acidosis. I. Concentration of Hydrogen Carbonate in the Blood Plasma ; its Significance, and its Estimation as a Measure of Acidosis. DONALD D. VAN SLYKE and GLENN E. CULLEN (*J. Biol. Chem.*, 1917, **30**, 289—346).—The work recorded in this and subsequent papers is based on the following hypothesis. Free carbon dioxide is present in the fluids of the body in such concentration that it automatically converts into hydrogen carbonate all bases not bound by other acids. The hydrogen carbonate, therefore, represents the excess of base which is left after all the non-volatile acids have been neutralised, and is available for the immediate neutralisation of further acids. In this sense it constitutes the "alkaline reserve" of the body. The concentration of hydrogen carbonate in the blood is representative of that in the body fluids in general, and is normally maintained at a constant level. Entrance of free acids reduces it to an extent proportional to the amount of the invading acid. Acidosis, therefore, is defined as a condition in which the concentration of hydrogen carbonate in the blood is reduced below the normal level.

The authors describe a method for estimating the concentration of hydrogen carbonate in the blood plasma under standard conditions. The plasma, from oxalated blood, drawn and centrifugalised under definite conditions, is shaken at the ordinary temperature in a separating funnel filled with alveolar air from the lungs of the operator or with an artificial air mixture containing 5.5% of carbon dioxide. The carbon dioxide in the plasma is then estimated by the method subsequently described (this vol., ii, 422). The results are calculated in terms of hydrogen carbonate by the aid of a table included in the text.

The average amount of carbon dioxide present as hydrogen carbonate in the plasma of normal men, estimated under the standard conditions, is 65 c.c. per 100 c.c. of plasma, the extreme limits being 77 and 53 respectively. In acidosis, the value obtained falls below normal, and is less the greater the severity of the prevailing acidosis condition. The method therefore constitutes a most sensitive indicator of this condition and can readily be applied clinically.

Experiments are also described showing the influence on the hydrogen carbonate of the plasma of various factors, in particular of the shift of bases and acids between plasma and corpuscles, under the influence of changing concentration of carbon dioxide in the blood.

H. W. B.

Acidosis. III. Electrometric Titration of Plasma as a Measure of its Alkaline Reserve. GLENN E. CULLEN (*J. Biol. Chem.*, 1917, **30**, 369—388. Compare van Slyke and Cullen, preceding abstract).—The method described is based on the hypothesis

that when a given amount of acid is added to a given volume of blood or plasma, the resultant change in the hydrogen-ion concentration (C_H) will be greater the less the alkaline reserve, or conversely, that when the alkaline reserve is low, less acid is necessary to produce a given increase in C_H . The amount of carbon dioxide in the plasma is first brought to a constant level by shaking with a known volume of air. It is then treated with an equal volume of $N/50$ -hydrochloric acid, and the concentration of hydrogen ion estimated by the gas chain method. In an alternative procedure, the influence of carbon dioxide is removed by adding 2 volumes of $N/50$ -hydrochloric acid to the plasma and exhausting the solution before estimating the hydrogen-ion concentration. The results obtained from the two procedures are different, but run parallel under varying conditions (compare Stillman and collaborators, this vol., i, 523) with the capacity of the plasma for combining with carbon dioxide. The electrometric titration constitutes, therefore, a trustworthy index of the alkaline reserve actually existing in the body.

H. W. B.

Acidosis. IV. Relationship between Alkaline Reserve and Acid Excretion. REGINALD FITZ and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1917, **30**, 389—400. Compare preceding abstract).—The introduction of an acid into the circulatory system immediately reduces the amount of alkali hydrogen carbonate in the blood, and is followed by an increased rate of excretion of ammonium salts, acid phosphates, and other acid substances in the urine. The authors find that this relationship is quantitative and can be expressed empirically by a formula similar to that devised by Ambard to denote the relationship between blood concentration and excretion in the cases of salt and urea. If D represents the rate of excretion of ammonia plus titratable acid, expressed as the equivalent number of c.c. of $N/10$ -acid passed in twenty-four hours, C the concentration of ammonia plus titratable acid in the urine, also expressed in c.c. of $N/10$ -acid per litre, and W the body-weight in kilograms, then the volume of carbon dioxide in 100 c.c. of the blood plasma, estimated by van Slyke's method, is $80 - \sqrt{(D/W \cdot \sqrt{C})}$. The data can be estimated by analysis of the urine passed in twenty-four hours or from the amount excreted in one or two hours, multiplied to bring it to the twenty-four-hour basis. The results are accurate within 10 volumes per cent. The calculation is simplified by the use of a series of curves given in the text, by means of which the index can be read off at once when the volume of urine passed per kilogram of body-weight per twenty-four hours and the amount of ammonia plus titratable acid per litre of the urine are known.

This relationship holds in the case of diabetics as well as of normal persons, but diabetics receiving carbonate administrations are exceptions, the carbon dioxide in the plasma being, as a rule, much higher than that calculated from the urinary analysis.

H. W. B.

Acidosis. V. Alveolar Carbon Dioxide and Plasma Hydrogen Carbonate in Normal Men during Digestive Rest and Activity. DONALD D. VAN SLYKE, EDGAR STILLMAN, and GLENN E. CULLEN (*J. Biol. Chem.*, 1917, **30**, 401—404. Compare A., 1915, i, 733, and preceding abstracts).—In the normal person, the volume of carbon dioxide present as hydrogen carbonate in 100 c.c. of blood plasma varies between 53 and 78 c.c. The ratio of plasma hydrogen carbonate to alveolar carbon dioxide tension, measured in millimetres of mercury, varies from 1.27 to 1.80. The alveolar carbon dioxide tension rises after a meal, whilst the plasma hydrogen carbonate sometimes slightly increases and at other times remains unchanged. The change in alveolar carbon dioxide after a meal is therefore probably due to an action on the respiratory centre (Higgins, A., 1914, i, 613) and not to a change in the hydron concentration of the blood due to the secretion of gastric juice (*loc. cit.*).
H. W. B.

Acidosis. VI. Blood, Urine, and Alveolar Air in Diabetic Acidosis. EDGAR STILLMAN, DONALD D. VAN SLYKE, GLENN E. CULLEN, and REGINALD FITZ (*J. Biol. Chem.*, 1917, **30**, 405—456. Compare preceding abstracts).—The authors have measured the alveolar carbon dioxide tension, the carbon dioxide present as hydrogen carbonate in the blood and in the blood plasma, the hydrogen-ion concentration of the plasma, and the index of acid excretion in the urine in a number of diabetics. Curves are drawn indicating the variations in these factors from day to day, and it is noted that there is a general parallelism between all the curves. The agreement between the factors relating to the urine and blood is on the average more accurate than that of the alveolar air and blood, and is observed, not only in adults, but also in children of as little as 25 kilograms of body-weight. In very severe acidosis, however, the urine index is less accurate than the alveolar air in indicating the alkaline reserve.

The results indicate the existence of the following relations between the intensity of the acidosis and the volume of carbon dioxide in c.c. present as hydrogen carbonate in 100 c.c. of blood plasma: normal resting adult, 77—53; mild acidosis, 53—40; moderate acidosis, 40—30; severe acidosis with symptoms of acid intoxication, below 30. The lowest volume of carbon dioxide recorded in which recovery occurred is 16.
H. W. B.

Non-protein Nitrogen of Blood: 1. Removal of the Protein. 2. Estimation of Creatine. ISIDOR GREENWALD (*Proc. Soc. exp. Biol. Med.*, 1917, **14**, 115—117. Compare A., 1916, ii, 62).—Blood is run into boiling 0.01*N*-acetic acid, and the last traces of protein are removed by thoroughly shaking the filtrate (from the coagulum) with kaolin. Kaolin also quantitatively adsorbs creatinine, but creatine not at all. By evaporating the filtrate from kaolin with acid (filtrate from 50 c.c. of blood with 10 c.c. of *N*-hydrochloric acid to a volume of 5—10 c.c.), a solution is obtained giving with picric acid a solvent reaction like that of crea-

tinine and corresponding with 4 mg. of creatine per 100 c.c. of blood. It is not certain whether the reaction is indeed due to creatinine, but added creatine is quantitatively accounted for. G. B.

Chemical Evidence of the Presence of Glycogen-like Polysaccharide in the Liver-blood of Diabetic Animals.

J. J. R. MACLEOD (*Proc. Soc. exp. Biol. Med.*, 1917, 14, 124—125).—In hyperglycæmic and diabetic dogs and rabbits the blood from the liver contains a polysaccharide, giving a reddish-violet colour with iodine and precipitated by alcohol and sodium chloride. On hydrolysis, a reducing sugar is formed. The amount is very small. G. B.

A Study of Methods of Estimation of Metabolic Nitrogen.

E. B. FORBES, C. E. MANGELS, and L. E. MORGAN (*J. Agric. Research*, 1917, 9, 405—411).—Five pigs were fed on a basal ration of corn, supplemented in succeeding periods with dried blood, skim milk, and egg-albumin. The metabolic nitrogen was determined in the fæces from these periods by three methods, namely: (1) the acid-pepsin method; (2) the acid-pepsin and alkaline-pancreatin method; (3) Jordan's method, consisting of successive extractions with ether, boiling alcohol, boiling water, and cold saturated calcium hydroxide solution. The apparent digestibility of the protein of the corn was 75%. Allowing for the metabolic nitrogen, the real digestibilities obtained were, by method (1) 92%, by method (2) 96%, and by method (3) 86%. All three methods make the nitrogen of blood albumin appear more than completely digestible, the feeding of blood albumin apparently increasing the digestibility of the corn protein. In comparing the three methods, it seems probable that methods (1) and (2) give results which are more nearly true than those from Jordan's method, which does not digest bacteria. W. G.

Nutrition Investigations on Cotton-seed Meal. II.

ANNA E. RICHARDSON and HELEN S. GREEN (*J. Biol. Chem.*, 1917, 30, 243—258. Compare A., 1916, i, 581).—The results previously obtained (*loc. cit.*) are confirmed. Normal growth and reproduction are observed in the case of albino rats on a diet containing 50% of cotton-seed flour, provided sufficient butter fat and protein-free milk are also administered. Toxic effects are not observed even in feeding 50% of cotton-seed flour to rats through four successive generations, but small amounts of crystallised gossypol prepared from cotton-seed kernels cause rapid loss in weight and death of the animals. H. W. B.

Biological Efficiency of Potato Nitrogen.

MARY S. ROSE and LENA F. COOPER (*J. Biol. Chem.*, 1917, 30, 201—204).—Nitrogenous equilibrium can be maintained on a diet in which potato constitutes practically the sole source of protein. H. W. B.

Rôle of Yeast in the Nutrition of an Insect (*Drosophila*).

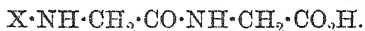
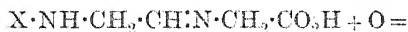
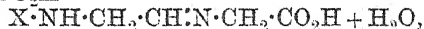
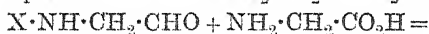
J. H. NORTHPROP (*J. Biol. Chem.*, 1917, **30**, 181—187. Compare Loeb and Northrop, this vol., i, 65).—Experiments are described the results of which indicate that yeast contains a sufficient excess of accessory substances to render available for the nutrition of the banana fly approximately twice as much food material as is contained in the yeast. For instance, the rate of growth of the larvæ is equally rapid on mixtures of banana and yeast containing 33% or more of yeast as it is on yeast alone. In mixtures containing less than this proportion of yeast, growth becomes slower as the percentage of yeast is decreased, and finally, when the proportion of yeast is very small, becomes abnormal. Casein and sugar may serve as adequate food material for growing larvæ provided a sufficient proportion of yeast is also present.

Various tissues have been employed as the sole source of nutritive material for the growing larvæ; the kidney, liver, and pancreas of the dog, liver from the mouse, and the bodies of the flies themselves are found to permit of normal growth, whilst the spleen, muscle, blood, adrenal and thyroid glands from the dog and the muscle and testis from the mouse are inadequate. The larvæ grow normally on any tissues when they are infected with bacteria. Certain tissues therefore contain the requisite accessory substances which are absent from others.

H. W. B.

Synthesis of Peptides in the Animal Organism. HERMANN

PAULY (*Zeitsch. physiol. Chem.*, 1917, **99**, 161—165).—The author suggests that in the animal organism the combination of amino-acids to form peptides, and eventually proteins, does not occur directly, but by a succession of reductions and oxidations. An amino-acid is readily reduced to an aldehyde, and if combination with another amino-acid should ensue, the resulting compound on oxidation should yield a peptide in accordance with the following equations: $X \cdot NH \cdot CH_2 \cdot CO_2H + H_2 = X \cdot NH \cdot CH_2 \cdot CHO + H_2O$,



The last reaction involves the oxidation of the group $\cdot CH \cdot N \cdot$ to $\cdot C(OH) \cdot N \cdot$, followed by tautomeric change to $\cdot CO \cdot NH \cdot$.

In support of his views, the author finds that when neutral aqueous solutions of benzaldehyde and glycine are mixed and oxidised at the ordinary temperature with potassium permanganate, a small proportion of hippuric acid is produced.

H. W. B.

The Cerebrosides of Brain Tissue. P. A. LEVENE and C. J.

WEST (*Proc. Soc. exp. Biol. Med.*, 1917, **14**, 93—95).—The authors now accept the nomenclature of Thudichum. In confirmation of previous work (compare also Rosenheim, A., 1916, i, 493), it is held that the only point of difference in the

composition of the dextrorotatory phrenosin and the levorotatory kersin is in the nature of one component, namely, the fatty acid. Following a suggestion of Rosenheim, an unsuccessful attempt was made to separate phrenosin and kersin by means of the different solubility of their benzoyl derivatives, but it is hoped that a repeated benzoylation of the levorotatory fraction may finally lead to a successful separation of kersin. By a new method of hydrolysis, the previous statements as to the percentage of galactose in the substances were confirmed.

G. B.

Enzyme and Reaction of Medium in Autolysis. MAX MORSE (*J. Biol. Chem.*, 1917, **30**, 197—199).—In the autolysis of the liver of the guinea-pig, the proteolytic enzyme is active only when the medium is acid.

H. W. B.

The Active Principle of the Pituitary Gland. M. GUGGENHEIM (*Biochem. Zeitsch.*, 1917, **81**, 274—277).—A reply to the criticism of the author's work by Fühner (A., 1916, i, 778).

S. B. S.

Thermal Decomposition of the Active Principle of the Pituitary Gland. H. S. ADAMS (*J. Biol. Chem.*, 1917, **30**, 235—242).—The active principle contained in an extract of the pituitary gland is rapidly destroyed at 100° when the hydrogen-ion concentration of the solution is of the order of $N \times 10^{-5}$. The destruction proceeds in a manner characteristic of a single substance, decomposing according to the law for a unimolecular reaction, and is not accelerated by oxygenation. When the hydrogen-ion concentration is increased to $N \times 10^{-3}$, the active principle becomes stable. It is suggested that the active principle evoking the contraction of the uterus may be a different substance from that which produces the characteristic pressor effect of pituitary extracts.

H. W. B.

Influence of Protein Intake on Creatine Excretion in Children. W. DENIS and J. G. KRAMER with ANNA S. MINOT (*J. Biol. Chem.*, 1917, **30**, 189—196).—The results of feeding experiments on five children show that the amount of creatine found in the urine of children is directly dependent on the intake of protein, being high when large quantities of protein (creatine-free) are ingested, decreasing, and in some cases disappearing entirely, when the child is fed on a relatively low protein diet. Creatinuria in normal children is therefore due to the relatively high protein intake, which is the rule with practically all children. This condition is probably to be traced to the low saturation point of immature muscle for creatine revealed by the small creatine content of the muscles of children.

Since excessive protein katabolism in adults is attended with creatinuria (Denis, this vol., i, 496), and it has been shown that in pathological conditions urinary creatine is of exogenous origin (Denis, this vol., i, 367), it appears that the connexion between

creatinuria and protein metabolism is finally established (Folin and Denis, A., 1912, ii, 465). H. W. B.

Toxicity of Various Benzene Derivatives to Insects.

WILLIAM MOORE (*J. Agric. Research*, 1917, 9, 371—381).—Twenty-eight benzene derivatives (benzene, toluene, xylene and their chloro-, bromo-, iodo-, and nitro-derivatives, phenol, cresols, aniline, benzaldehyde, etc.) have been examined and compared with carbon disulphide as to their toxicity to the house-fly. Determinations were made of the different fractions of a gram-molecule necessary to kill in 400 minutes five flies enclosed in a stoppered litre flask with the compound. All the benzene derivatives tested were found to be more toxic to insects, molecule for molecule, than carbon disulphide. Although certain indications were found as to the relationship of chemical composition and toxicity, these were outweighed by the effect of physical properties. Up to 250°, the higher the boiling point the more toxic was the compound to insects. That the toxicity is not connected with lipoid solubility is shown by the fact that lipoids are very soluble in the compounds with low boiling points and but sparingly so in the compounds with high boiling points. For practical purposes, compounds with low boiling points, although less toxic, may give better results owing to their greater volatility. W. G.

The Sensitiveness of Strains of Nagana towards Arsenic and Antimony. ERNST TEICHMANN (*Biochem. Zeitsch.*, 1917, 81, 284—318).—The author draws the following conclusions from a large amount of experimental material, which is given in detail. Different strains of *Nagana* obtained from East Africa show marked differences in their sensitivity to arsacetin when this drug is employed both prophylactically and therapeutically. One particular strain which has long been kept in European laboratories was quite insensitive to arsenic. This was also the case for derivatives of this strain which had become fast towards the antibody. Similar differences in sensitivity were shown both by West and East African strains towards potassium antimonyl tartrate. In the case of this drug, the prophylactic treatment showed better results than the therapeutic. For curative treatment, arsacetin was more effective in the case of East African *Nagana* than potassium antimonyl tartrate. Each strain behaved differently, however, towards antimony and arsenic compounds as regards prophylactic and therapeutic action. There was no relationship between the virulence of a strain and its sensitivity towards the drugs. S. B. S.

Colloidal Nature of the Wassermann Reaction. R. M.

WALKER (*J. Path. Bact.*, 1917, 21, 184—192).—The author adduces evidence in support of the view that the fixation of complement is an adsorption by a colloidal complex formed from the antigen and the syphilitic serum. Normal serum does not confer

this property of selective adsorption on the antigen (compare Poyarkov, this vol., i, 427). G. B.

Comparison of the Actions of *d*, *l*, and *i*-Camphor.
I. Toxicity to Cats. II. Action on the Frog's Heart.
III. Antiseptic Action. GEORG JOACHIMOGLU (*Arch. exp. Path. Pharm.*, 1916—1917, **80**, 1—7, 259—281, 282—287).—In contradistinction to hyoscyamine, adrenaline, etc., there is no difference in the physiological action of the enantiomorphs. The investigation was suggested by the present shortage of *d*-camphor in Germany. G. B.

Peptone Hypoglycæmia. HUGH MCGUIGAN and E. L. ROSS (*J. Biol. Chem.*, 1917, **30**, 175—179. Compare A., 1915, i, 1038).—The authors confirm previous results showing the production of hypoglycæmia in dogs after the intravenous injection of peptone solutions. H. W. B.

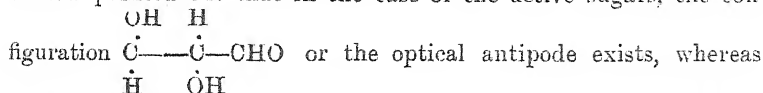
Chemistry of Vegetable Physiology and Agriculture.

Nitrogenous Food Requirement of some of the Commoner Pathogenic Bacteria. M. H. GORDON (*J. Roy. Army Med. Corps*, 1917, **28**, 371—376).—Considerable differences exist. With dextrose as source of carbon, *B. coli*, *B. paratyphosus*, *B. pyocyaneus*, and *B. proteus* can satisfy their nitrogen requirements with ammonium salts and some of the simpler amides and amino-acids. *B. diphtheriae* and *B. pseudodiphtheriae*, Staphylococci, and Streptococci require more complex compounds. The cholera vibrio and *B. dysenteriae* can live on asparagine, but not on ammonium salts. G. B.

Improved Chemical Methods for Differentiating Bacteria of the Coli-aerogenes Family. WILLIAM MANSFIELD CLARK and HERBERT A. LUBS (*J. Biol. Chem.*, 1917, **30**, 209—234).—The classification of bacteria of the coli-aerogenes family by means of the Clark-Lubs methyl-red test is facilitated by using a medium containing 0.7% of anhydrous disodium hydrogen phosphate, 0.2% of potassium hydrogen phthalate, 0.1% of aspartic acid, and 0.4% of dextrose. H. W. B.

The Formation of Ferments. III. MARTIN JACOBY (*Biochem. Zeitsch.*, 1917, **81**, 332—341).—In the first communication (this vol., i, 305) it was shown that *d*-glucose, *d*-galactose, and *d*- and *l*-arabinose contribute to the formation by bacteria of the urease ferment, whilst *d*-mannose and rhamnose are inactive. It

is now pointed out that in the case of the active sugars, the con-



in the case of the inactive sugars, the hydroxyl groups or hydrogen atoms are on the same side of the carbon atoms contiguous to the aldehyde group.

In continuation of the work described in the second communication (this vol., i, 430), it is now shown that the addition of edestin, but not of caseinogen, to Uschinski's medium promotes the formation of the urease. The addition of glycine, alanine, tyrosine, or valine was without effect. It has already been shown that addition of bouillon from horse-meat to Uschinski's medium promotes the formation of the urease. It was also found that culture on medium from certain bouillon tablets promotes ferment formation, and that the further addition of amino-acids accelerates this formation still more. The bouillon tablets also promote urease formation when added to Uschinski's medium. From the above-mentioned results, the conclusion is drawn that Uschinski's medium is wanting in amino-acids and some other substance which is contained in the bouillons and in the hydrolysis products of edestin. Further experiments showed that synthetic leucine had no effect on urease formation when added to Uschinski's medium, whereas pure *l*-leucine, and *d*- and *l*-isoleucine (obtained from F. Ehrlich), promoted the formation of the ferment. It has therefore been found possible to obtain the ferment when bacteria are grown on media containing only simple chemical substances. It is not clear from the author's statements why synthetic leucine is inactive.

S. B. S.

The Significance of Nitrification as a Factor in Soil Fertility. P. L. GAINES (*Soil Sci.*, 1917, 3, 399—416).—A very full résumé of the literature on the subjects of (*a*) the existence of active nitrifying organisms in cultivated soils, (*b*) the relation between ammonia content and nitrifying power of soils, (*c*) the relation between ammonia nitrogen content and crop yield. Certain new experimental data are given, and the author draws the general conclusion that whilst nitrification is perhaps a valuable and even essential asset in fertility, it probably does not, under normal conditions, become a limiting factor in productivity.

W. G.

The Extraction and Saturation of Soils with Volatile Antiseptics. J. P. DU BUISSON (*Soil Sci.*, 1917, 3, 353—392).—Two soils, both heavy loams, were subjected to partial sterilisation with the following antiseptics: alcohol, benzene, ether, toluene, and gasolene (light petroleum). The treatment was carried out in two ways: (1) by extracting the soils with the antiseptics, and (2) by merely saturating them, the soils being in both cases subsequently freed from the antiseptics by exposure to air. Pot

cultures of wheat and oats showed that all the above substances except gasoline could be used satisfactorily for partial sterilisation, alcohol giving the best results; also, that although the beneficial effect of sterilisation was still evident on a second crop, it was greatly diminished and varied somewhat with the nature of the soil under investigation. Portions of the same soils were incubated for a period of six months, and analysed for ammonia and nitric acid at intervals. Sterilisation inhibited nitrification and increased ammonification for a certain length of time, after which ammonification either decreased or remained constant, whilst nitrification became more active than in the untreated soil. Nitrification and ammonification tests carried out on the soils after they had been cropped once and twice confirmed the conclusion drawn from the pot experiments, and showed that the effect of sterilisation on the two above processes practically ceased after the first crop. Breaking up the soil and maintaining it in a loose condition did not increase the amount of ammonia and nitric nitrogen in the soil.

From the alcohol extracts of the soils a substance was recovered which proved toxic in water cultures. Extracted soils, however, did not give better results than saturated soils; in fact, the latter more usually yielded the larger plants. L. M. U.

Amygdalin as Nutriment for *Aspergillus niger*. II.

H. I. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 987—989. Compare this vol., i, 502).—Further experiments on the influence of amygdalin on the development of *Aspergillus niger* show conclusively that amygdalin is absorbed by the organism without any previous resolution into dextrose, benzaldehyde, and hydrogen cyanide. The experiments show that amygdalin diminishes the noxious influence of benzaldehyde. H. M. D.

Influence of Mineral Matters on the Germination of Peas.

L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1917, **165**, 45—51. Compare *ibid.*, **164**, 979).—Peas were germinated on sand moistened with water containing varying amounts of the salts examined, which were the chlorides of sodium, potassium, strontium, barium, manganese, and lead, and the sulphates of ammonium, calcium, magnesium, zinc, aluminium, and copper. The seeds were steeped for twenty-four hours and then allowed to germinate for six days, after which the length of the roots formed were measured. Calcium appears to be the only metal exerting any marked influence on the germination, the root length being markedly increased by the presence of as little as 0.01 mg. of calcium sulphate for each seed. As the amount of calcium salt is increased, the length of the root increases and the root hairs become more abundant. After calcium come strontium, manganese, aluminium, barium, and magnesium. Then come the alkali metals, zinc, lead, and copper, which has no immediate effect at the low concentrations, but appears to be toxic at a concentration of 0.1 mg. of anhydrous copper sulphate per seed. W. G.

Lævulose the Preponderant Sugar of Apple Juices.

JOHN R. EOFF, jun. (*J. Ind. Eng. Chem.*, 1917, 9, 587—588).—An examination of the relative proportions of sucrose, dextrose, and lævulose in the juices of twenty varieties of apples by a polarimetric method (Thompson and Whittier, Delaware Coll. Agric. Expt. Stat., 1913, Bull. 102) and a combined polarimetric-reducing power method (Browne, A., 1906, ii, 498). The results indicate that in every case the amount of lævulose exceeds the total quantity of other sugars present and confirms the earlier observations of Thompson and Whittier (*loc. cit.*), of Browne (A., 1902, ii, 371), and of Worcollier (*Ann. Falsif.*, 2, 425). D. F. T.

Secretions in the Rhizome of Rheum; a Contribution to the Microchemistry of the Hydroxymethylanthraquinone-bearing Plants. O. TUNMANN (*Ber. Deut. bot. Ges.*, 1917, 35, 191—203).—It not infrequently happens that when the rhizomes of Chinese rhubarb are split open, large, tumour-like growths are found imbedded in the normal tissue, separated completely by a layer of cork. Under what conditions these abnormal deposits are produced cannot be answered except by experiments on the living plant, but it is unlikely that the first cause is the boring in of insects. The author has, however, been able to determine the chief differences between the normal tissue and the enclosed growth, having at his disposal a specimen in which there were two such deposits, one inside the other, each bounded by cork tissue, the larger being nearly 5 cm. long.

The secretions consist of complex tissues which are practically free from starch, uncombined or glucosidic sugars, but rich in the usual oxalate druses. As the starch-bearing parenchyma is empty, this tissue is greatly compressed, and the oxalate cells appear to be abnormally numerous. Catechol and gallic acid are present in the woody fibres in undiminished quantity. Likewise, the residues of the anthraquinone-glucosides, namely, the hydroxymethyl-anthraquinones, are present in large quantities, but largely as the corresponding anthranols. These reduction products can be obtained by micro-sublimation, and recognisable nitro-compounds of the hydroxymethylanthraquinones can also be prepared on a microscope slide by warming a section of the growth with pure nitric acid. J. C. W.

Action of Coal Gas on Plants. II. Action on Green Plants.

C. WEHMER (*Ber. Deut. bot. Ges.*, 1917, 35, 318—332. Compare this vol., i, 507).—It is usually affirmed that coal gas is poisonous to green plants even when the atmosphere contains only minute quantities, but cress is remarkably resistant to its influence. The seedlings will grow unchecked in an atmosphere containing as much as 30% of gas, but they die in a short time if exposed to undiluted gas. The seeds themselves are not killed by coal gas, but only prevented from germination. The ill-effects of pure coal gas are not entirely due to the lack of oxygen, for cress will keep fresh and green in pure hydrogen for a much longer time than in coal gas. Experiments designed to elucidate the nature of the

particularly poisonous constituent of coal gas gave only negative results. Carbon monoxide, ethylene, and acetylene are not dangerous, even in concentrations much higher than those in which they commonly occur in coal gas. Benzene vapour, carbon disulphide, and hydrogen sulphide are very toxic, but not in the concentration met with in coal gas. The really toxic constituent is probably among the minor impurities. J. C. W.

The Aldehydes of Wines. J. LABORDE (*Ann. Inst. Pasteur*, 1917, 31, 215—252).—A comprehensive study of the catalytic and physiological agents causing aldehyde formation in wines. These agents exercise their influence principally on the young wines during their storage in barrels, which helps more or less the contact of the wine with atmospheric oxygen. The three principal catalytic agents promoting aldehyde formation are: (1) the tannin substances, more or less combined with potassium hydroxide; (2) cenoxydase; (3) the oxydase of *Botrytis cinerea*. Pasteurisation of normal wines, as well as the addition of sulphurous acid, checks aldehyde formation without completely preventing it. Pasteurisation behaves similarly with "cassable" wines, but in this case sulphurous acid favours aldehyde formation, whilst preventing the "cassee." There are equally important opposing influences which may lead to the complete disappearance of aldehyde from the wine if it is stored in the absence of air, and on this account but small amounts of aldehydes are to be found in red wines stored normally. In the case of "cassable" wines, the aldehyde plays no part, since it is only formed after marked oxidation of the tannin substances. Aldehyde formation opposed by aldehyde destruction has only a passing influence, although always unfavourable, on the bouquet of red wines in casks.

Of the micro-organisms which live in wine, only the facultative aerobic organisms (different yeasts) and the strictly aerobic organisms (mycoderma) produce aldehyde, although certain anaerobic ferments apparently yield acetaldehyde by attacking the glycerol of the wine. The yeasts and anaerobic microbes secrete reductases in the wine, which can contribute to the complete removal of aldehydes in wine, kept out of contact with air, unless the aldehydes are combined with sulphurous acid. W. G.

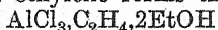
Investigation of Soil Excrecences. H. PUCHNER (*Kolloid Zeitsch.*, 1917, 20, 209—238).—The author discusses the formation of salt layers on the surface of various natural or artificial substances as the result of weathering, the immediate cause of the production of these efflorescences or excrecences being the removal of water by evaporation.

Experiments are described which show that the growth of these superficial layers is very appreciably influenced by the nature of the soil or other substance in which the salt is present. The general appearance and the crystalline structure of the separated salt is not only affected by the presence of colloidal humus substances, but also by the fineness of the soil particles. H. M. D.

Organic Chemistry.

Action of Anhydrous Aluminium Chloride [and Ferric Chloride] on Unsaturated Organic Compounds. II. WILMER C. GANGLOFF and W. E. HENDERSON (*J. Amer. Chem. Soc.*, 1917, **39**, 1420—1427. Compare A., 1916, i, 593).—Further compounds of aluminium and ferric chlorides with unsaturated hydrocarbons, acids, alcohols, and aldehydes are described, and their bearing on the use of these catalysts in the cracking of petroleum is discussed.

Acetylene gives the compounds $\text{AlCl}_3 \cdot \text{C}_2\text{H}_2 \cdot 2\text{EtOH}$ and $\text{AlCl}_3 \cdot \text{C}_2\text{H}_2 \cdot \text{MeOH} \cdot \text{H}_2\text{O}$; ethylene forms the compounds



and $\text{AlCl}_3 \cdot \text{C}_2\text{H}_4 \cdot \text{MeOH} \cdot \text{H}_2\text{O}$; γ -butylene yields the granular product $\text{AlCl}_3 \cdot \text{C}_4\text{H}_8 \cdot 2\text{MeOH} \cdot \text{H}_2\text{O}$; β -isoamylene gives a series of bright-coloured tars according to the amount of aluminium chloride, but an alcoholic solution yields the crystalline compound $\text{AlCl}_3 \cdot \text{C}_5\text{H}_{10} \cdot \text{CHMe} \cdot \text{MeOH}$; styrene forms the sweet-smelling compounds $\text{AlCl}_3 \cdot \text{C}_8\text{H}_8$ and $\text{AlCl}_3 \cdot 2\text{C}_8\text{H}_8 \cdot 2\text{H}_2\text{O}$.

Oleic acid forms an asphalt-like mass, but if diluted with methyl alcohol, a compound, $4\text{AlCl}_3 \cdot \text{C}_{18}\text{H}_{34}\text{O}_2$, resembling brown sugar, may be isolated. Fumaric acid yields a snow-white compound, $\text{AlCl}_3 \cdot \text{C}_4\text{H}_4\text{O}_4$, which sublimes unchanged at 200° . A methyl-alcoholic solution of furfuraldehyde gives a crystalline, coal-like product, $\text{AlCl}_3 \cdot \text{C}_5\text{H}_4\text{O}_2 \cdot \text{MeOH}$, and a solution of benzaldehyde forms a pale yellow, crystalline compound, $\text{AlCl}_3 \cdot \text{C}_7\text{H}_6\text{O} \cdot \text{MeOH}$. Diluted allyl alcohol yields the pungent-smelling compound $\text{AlCl}_3 \cdot \text{C}_3\text{H}_6\text{O} \cdot \text{MeOH}$.

Anhydrous ferric chloride reacts with methyl-alcoholic solutions of amylene and furfuraldehyde to form the compounds $\text{FeCl}_3 \cdot \text{C}_5\text{H}_{10} \cdot \text{MeOH}$ and $\text{FeCl}_3 \cdot \text{C}_5\text{H}_4\text{O}_2 \cdot \text{MeOH}$ respectively.

The yields of benzophenone obtained in the condensation of benzoyl chloride with benzene under the influence of various anhydrous metallic chlorides have been roughly determined. Under similar conditions, aluminium chloride gave 70—71%, ferric chloride 60—62%, zinc chloride 28—32%, chromic and cuprous chlorides nil.

J. C. W.

Preparation of Ethylene Glycol. BENJAMIN T. BROOKS and IRWIN HUMPHREY (*J. Ind. Eng. Chem.*, 1917, **9**, 750—751).—One mol. of ethylene dichloride, 5 volumes of methyl alcohol, and 3 mols. of sodium formate are heated together at 165° to 170° in an autoclave for seven hours. After cooling, the methyl alcohol solution is separated from the salts and distilled. The methyl alcohol may be distilled at ordinary pressure and the glycol under reduced pressure. Ethylene dichloride is readily prepared by the action of chlorine on ethylene at 0° ; if the mixture becomes heated, large quantities of trichloroethane are formed. The gases should not be dried.

W. P. S.

Preparation of β -Chloro- and β -Bromopropionic Acids.

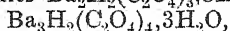
WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1465—1466).—Ethylene chlorohydrin is dissolved in alcohol, concentrated potassium cyanide solution is gradually added to the boiling solution, and after some hours the cyanohydrin is isolated and distilled (b. p. $110^{\circ}/15$ mm.). On hydrolysis with hydrochloric or hydrobromic acid, β -chloro- or β -bromopropionic acid is obtained in good yield, replacement of the hydroxyl group by halogen taking place simultaneously.

J. C. W.

Hydrogen Oxalates of the Alkali Earth Metals. G.

BRUHNS (*Zeitsch. anorg. Chem.*, 1916, **95**, 194—224).—In view of the uses of oxalic acid in analysis, and of the advantages of pure oxalic acid as a standard for volumetric solutions (A., 1916, ii, 158, 533), the conditions under which acid salts of the alkali earths are formed have been investigated.

Dilute solutions of barium chloride yield with 2 mols. of oxalic acid a crystalline precipitate of the salt $\text{BaH}_2(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, which is rapidly decomposed by cold water. $1\text{H}_2\text{O}$ is readily lost, even at atmospheric temperature in a vacuum, whilst the other molecule is only driven off at 125° . Solutions of progressively diminishing acidity yield the salts $\text{Ba}_2\text{H}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ and



all being similar in appearance.

Titration with $N/10$ -sodium hydroxide shows that a small part of the oxalic acid remains combined with the normal oxalate, even after prolonged boiling. When barium hydroxide solution is in excess, the precipitated barium oxalate contains an excess of barium. The error in titrating barium with oxalic acid, and conversely, is therefore considerable.

Normal barium oxalate may contain more than $1\text{H}_2\text{O}$ when precipitated cold from barium hydroxide and oxalic acid, whilst the product from barium chloride and sodium oxalate may contain less than 1 mol., even from dilute solution. At 100° it only contains $\frac{1}{2}\text{H}_2\text{O}$.

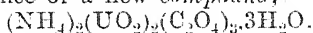
Strontium has less tendency to form acid salts. A salt, $\text{Sr}_2\text{H}_2(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$, is obtained which is decomposed completely by cold water. Slow crystallisation from slightly acid solution, however, yields homogeneous crystals containing an excess of acid which are only very slowly decomposed by water. Strontium chloride is more suitable than calcium chloride for addition in the titration of oxalic acid under conditions which cause rapid precipitation. A $N/10$ -solution of strontium hydroxide is very suitable for volumetric estimations of oxalic acid, care being taken that the alkaline solution is not in excess, which would cause the precipitate to retain strontium. The water of crystallisation varies, as in the case of other oxalates, with the conditions of preparation.

The titration of oxalic acid in nitric acid solution is quite satis-

factory in the presence of barium nitrate, and even of barium chloride. C. H. D.

The System Water-Uranyl Oxalate-Ammonium Oxalate.

A. COLANI (*Compt. rend.*, 1917, **165**, 234—236).—An examination of the solubility curves of the system water-uranyl oxalate-ammonium oxalate at 15°, 50°, and 75° confirms the results of Rosenheim and Lienau (compare A., 1899, i, 569) and Wyruboff (compare *Bull. Soc. Franc. Min.*, 1909, **32**, 351) as to the existence of the complex $(\text{NH}_4)_3(\text{UO}_2)(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, and of Wyruboff (*loc. cit.*) of the complex $(\text{NH}_4)_4(\text{UO}_2)(\text{C}_2\text{O}_4)_3$, and in addition indicates the existence of a new compound,



At 50° only the anhydrous salts are formed, and the salt $(\text{NH}_4)_4(\text{UO}_2)(\text{C}_2\text{O}_4)_3$ is only formed at 60° or above. W. G.

Oxidation of the Alkali Butyrates by Hydrogen Peroxide with the Production of Succinic Acid.

EDWARD CAHEN and WILLIAM HOLDSWORTH HURTLEY (*Biochem. J.*, 1917, **11**, 164—171).—When sodium butyrate and hydrogen peroxide in aqueous solution are heated together at 65°, succinic acid is produced, and may amount to as much as 50% of the oxidised butyrate. When the amount of hydrogen peroxide is relatively increased, the yield of succinic acid is diminished, whilst that of carbon dioxide is enormously increased. Under the conditions observed, the fatty acid is attacked at the methyl group at the end of the carbon chain instead of at the α - and β -carbon atoms, as found in the experiments of Dakin (A., 1908, i, 74).

H. W. B.

Crystallographic Investigations of the Succinic Acids, their Homologues and Derivatives.

ANTON STEFL (*Zeitsch. Kryst. Min.*, 1914, **54**, 343—387).—The object of this work was to investigate the crystallographic relationships between geometrically isomeric acids and their derivatives. It has also been extended to include the glutaric and mesaconic acids and their derivatives.

Succinic acid forms monoclinic plates or prisms, varying in habit according to the solvent, water, acetone, ethyl acetate, etc. [$a:b:c=0.5747:1:0.8581$; $\beta=133^\circ 37'$]. Cleavage and optic axial plane, {010}; D 1.577; M.V. 74.81.

cis-s-Dimethylsuccinic acid, monoclinic prisms from water or ethyl acetate [$a:b:c=0.6967:1:0.8549$; $\beta=93^\circ 9\frac{1}{2}'$]; D 1.349(7); M.V. 110.69. Cleavage and optic axial plane, {010}.

trans-s-Dimethylsuccinic acid, triclinic plates from ether [$a:b:c=0.8485:1:0.8944$; $\alpha=97^\circ 54\frac{1}{2}'$; $\beta=125^\circ 9\frac{1}{2}'$; $\gamma=89^\circ 47\frac{1}{2}'$]. Cleavage plane, {010} perfect; {110} and {110} less good. D 1.349; M.V. 110.72.

as-Dimethylsuccinic acid, prepared by Bone and Sprankling's method (T., 1899, **75**, 858), forms triclinic prisms from acetone

$[a:b:c=1.1265:1.20244; \alpha=78^{\circ}40'; \beta=105^{\circ}30'; \gamma=112^{\circ}8\frac{1}{2}']$.
Cleavage, {010} and {110}; D 1.323; M.V. 110.38.

Trimethylsuccinic acid, rhombic prisms from water, alcohol, ether, or amyl acetate $[a:b:c=0.6585:1.08297]$. Cleavage {010} and {110}; optic axial plane {100}; D 1.242(5); M.V. 128.77.

Tetramethylsuccinic acid, from ether or acetone, forms both monoclinic and triclinic crystals; from aqueous methyl alcohol, light petroleum, or ethyl acetate only triclinic.

Monoclinic form: $[a:b:c=1.0923:1.07208; \beta=100^{\circ}26']$; cleavage {100} and {010}; D 1.300; M.V. 133.85.

Triclinic form: $[a:b:c=0.7556:1.20168; \alpha=89^{\circ}42'; \beta=101^{\circ}39'; \gamma=89^{\circ}33']$; cleavage {110} and {110}; D 1.300.

n-s-Dimethyldiethylsuccinic acid, triclinic prisms, pseudo-hexagonal with respect to the axis *b*, from acetone solution $[a:b:c=0.8499:1.08954; \alpha=97^{\circ}50'; \beta=124^{\circ}25'; \gamma=90^{\circ}0']$; cleavage perfect on {010}, poor on {01}; D 1.247; M.V. 161.95.

Glutaric acid, thin, monoclinic, six-sided plates from acetone $[a:b:c=2.0737:1.35359; \beta=131^{\circ}36']$; cleavage {100} and {110}; optic axial plane {010}; D 1.427; M.V. 92.50.

Mesaconic acid, thin, four-sided plates from ether, monoclinic (sphenoidal?) $[a:b:c=0.5933:1.12632; \beta=108^{\circ}34']$; cleavage {100}; optic axial plane {010}; D 1.466; M.V. 88.68.

Tetramethylsuccinodinitrile, monoclinic plates from ether, alcohol, etc. $[a:b:c=0.6890:1.07109; \beta=116^{\circ}25']$; cleavage and optic axial plane, {010}; D 1.070; M.V. 127.1.

s-Dimethyldiethylsuccinodinitrile, triclinic plates $[a:b:c=0.4947:1.05913; \alpha=99^{\circ}54'; \beta=110^{\circ}41\frac{1}{2}'; \gamma=89^{\circ}7\frac{1}{2}']$; D 1.075(5); M.V. 152.5.

Tetraethylsuccinodinitrile, triclinic plates $[a:b:c=0.5109:1.1998; \alpha=80^{\circ}2'; \beta=110^{\circ}45'; \gamma=90^{\circ}40']$; D 1.076; M.V. 178.46.

Succinic anhydride, stable crystalline modification, forms rhombic, bipyramidal prisms $[a:b:c=0.5945:1.04603]$. Cleavage and glide plane, {101}; optic axial plane, {001}; D 1.503; M.V. 66.54.

cis-s-Dimethylsuccinic anhydride, monoclinic plates $[a:b:c=0.5859:1.16044; \beta=93^{\circ}31']$; D 1.337; M.V. 95.75.

Measurable crystals of the trans-isomeride of *as*-dimethylsuccinic and tetramethylsuccinic anhydrides could not be obtained.

s-Dimethyldiethylsuccinic anhydride, monoclinic prisms $[a:b:c=0.5900:1.09756; \beta=91^{\circ}29\frac{1}{2}']$; D 1.189; M.V. 154.7.

Tetraethylsuccinic anhydride, stout, monoclinic crystals from ether, alcohol, ethyl acetate, etc. $[a:b:c=0.8842:1.09052; \beta=95^{\circ}34\frac{1}{2}']$; D 1.207(8); M.V. 175.53.

Glutaric anhydride, long, flat, monoclinic prisms from ether $[a:b:c=1.4249:1.19623; \beta=91^{\circ}47']$; D 1.411; M.V. 80.81.

Succinimide, stable modification, rhombic, bipyramidal plates or prisms from acetone $[a:b:c=0.7888:1.13655]$; D 1.418; M.V. 71.42.

cis-s-Dimethylsuccinimide, thin, monoclinic plates [$a:b:c=0.9089:1:1.3153$; $\beta=100^\circ 10\frac{1}{2}'$]; cleavage, {001}; optic axial plane perpendicular to {010}; D 1.284; M.V. 98.91. The crystals of the trans-isomeride could not be measured.

as-Dimethylsuccinimide, six-sided, tabular, monoclinic crystals from ethyl acetate or alcohol [$a:b:c=2.0385:1:1.8937$; $\beta=120^\circ 37'$]; cleavage, {001}; optic axial plane, {010}; D 1.244; M.V. 102.04.

Trimethylsuccinimide, rhombic prisms, a combination of a rectangular prism with basal plane. The axial ratios could not be determined.

Tetramethylsuccinimide, thin, monoclinic plates or needles [$a:b:c=1.6255:1:2.0679$; $\beta=92^\circ 8'$]; D 1.185; M.V. 130.76.

s-Dimethyldiethylsuccinimide, monoclinic prisms [$a:b:c=0.5829:1:0.9773$; $\beta=91^\circ 32'$]; D 1.189(9); M.V. 153.79.

Tetraethylsuccinimide, triclinic tables [$a:b:c=0.8549:1:1.4893$; $\alpha=79^\circ 16'$; $\beta=105^\circ 52'$; $\gamma=86^\circ 55'$]; D 1.166; M.V. 180.99.

Glutarimide, rectangular, monoclinic tables from alcohol or ethyl acetate [$a:b:c=0.9849:1:1.3772$; $\beta=102^\circ 17'$]; cleavage, {001} and {100}; D 1.393; M.V. 81.12.

Citraconimide, monoclinic plates [$a:b:c=? : 1:1.3154$; $\beta=100^\circ 0'$]; cleavage, {100}; D 1.410; M.V. 78.72.

Succinochloroimide, rhombic plates (? bipyramidal) [$a:b:c=0.8949:1:1.6308$]; optic axial plane, {100}; D 1.650; M.V. 80.72.

Succinobromoimide, rhombic bisphenoidal crystals [$a:b:c=0.8994:1:1.6360$]; axial plane, {100}; D 2.098; M.V. 84.7.

Succinoiodoimide, ditetragonal bipyramidal [$a:c=1:0.8733$]; D 2.245; M.V. 100.16.

Tetramethylsuccinochloroimide, four-sided rhombic bipyramidal plates [$a:b:c=0.9848:1:1.3912$]; optic axial plane, {010}; D 1.303; M.V. 145.19.

Tetramethylsuccinobromoimide, isomorphous with the last [$a:b:c=0.9898:1:1.4650$]; optic axial plane, {100}; D 1.578; M.V. 147.88.

Tetramethylsuccinoiodoimide, rhombic pyramidal [$a:b:c=1.1051:1:0.8502$]; D 1.816; M.V. 154.69.

Succinanil, monoclinic tables [$a:b:c=2.1125:1:2.3065$; $\beta=101^\circ 42'$]; cleavage, {100}; optic axial plane, {010}; D 1.356; M.V. 129.75.

cis-s-Dimethylsuccinanil, rhombic bipyramidal prisms [$a:b:c=1.2568:1:2.6730$]; cleavage, {001}; D 1.253; M.V. 161.97.

trans-s-Dimethylsuccinanil, monoclinic plates [$a:b:c=1.3724:1:3.0810$; $\beta=116^\circ 17'$]; cleavage, {001}; optic axial plane, {010}; D 1.239; M.V. 163.84.

as-Dimethylsuccinanil, monoclinic needles [$a:b:c=2.3885:1:4.1003$; $\beta=97^\circ 1'$]; cleavage, {001}; optic axial plane, {010}; D 1.247; M.V. 162.73.

Trimethylsuccinanil, rhombic bipyramidal prisms [$a:b:c=1.6490:1:2.3204$]; cleavage, {001}; optic axial plane, {010}; D 1.240; M.V. 175.0.

Tetramethylsuccinanil, long, monoclinic prisms [$a:b:c=3.2444:1.63002$; $\beta=90^\circ 37'$]; cleavage, {001}; D 1.199; M.V. 192.58.

s-Dimethyldiethylsuccinanil, monoclinic prisms [$a:b:c=1.2882:1.24242$; $\beta=93^\circ 17\frac{1}{2}'$]; D 1.181; M.V. 219.3.

Glutaranil, monoclinic tables [$a:b:c=2.4120:1.24318$; $\beta=97^\circ 37'$]; cleavage, {100}; optic axial plane, {010}; D 1.304; M.V. 144.88.

Citraconanil, monoclinic thin needles or plates [$a:b:c=2.7652:1:2.8700$; $\beta=99^\circ 36'$]; optic axial plane, {010}; D 1.283; M.V. 145.75.

Those compounds having a cyclic structure show much closer crystallographic relationship among themselves than those having open-chain structures. There is not generally the close relationship between anhydrides and imides which might have been expected, but these derivatives of *s*-dimethyldiethylsuccinic acid are isomorphous. The entrance of a CH_3 group occasions less morphotropic change in the cyclic than in the open structures. Morphotropic relationships are clear among some of the halogen imides and among the anils.

E. H. R.

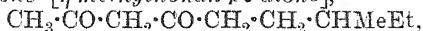
Two Isomeric Citronelaldehydes. H. J. PRINS (*Chem. Weekblad*, 1917, 14, 692—695).—By repeated fractionation, two isomerides have been isolated from citronelaldehyde. The first has b. p. 203—204°, D^{20}_D 0.8880, and forms a semicarbazone, m. p. 85—86°. The second has b. p. 198—200°, D^{20}_D 0.8745, and gives a semicarbazone, m. p. 82.5—83°. It is suggested that the first has the formula $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHO}$, and the second the formula $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHO}$.

A. J. W.

The Influence of Constitution on the Rotation of Optically-active Substances. X. Optically-active Ketones and Diketones. H. RUPE and SAMUEL WILD (*Annalen*, 1917, 414, 111—125).—As it is possible to obtain many saturated and unsaturated derivatives of ketones and aldehydes, the influence of constitution on the optical properties of active members of these classes can be investigated most advantageously. Not much is known concerning optically active ketones and aldehydes, but a beginning has now been made with derivatives of amylacetone (*ε*-methylheptan- β -one).

Ethyl amylacetoacetate, prepared from active amyl bromide and ethyl sodioacetoacetate, has b. p. 112°/10 mm., D^{20}_D 0.9513, $[\alpha]^{20}_D +13.66^\circ$, 14.11° in 10% benzene solution. The "characteristic wave-length," λ_c (see A., 1915, ii, 718) is 643.0 for the pure liquid and 592.3 for the 10% benzene solution. The inactive ester has the same b. p. Active *amylacetone* [*ε*-methylheptan- β -one] is obtained by hydrolysis with 12% methyl-alcoholic potassium hydroxide as a mobile oil, resembling amyl acetate; b. p. 70°/11 mm., D^{20}_D 0.8295, $[\alpha]^{20}_D +8.20^\circ$, 7.34° in 10% benzene, 8.09° in 10% alcohol, λ_c 664.2, 581.9 for benzene solution, 609.8 for alcoholic solution. The ketone condenses with benzaldehyde in the presence of sodium hydroxide to yield *benzylideneamylacetone* [α -benzyl-

idene-ε-methylheptan-β-one]; the *active* form crystallises in matted, silvery-white needles, m. p. 138°, $[\alpha]_D^{20} + 10.77^\circ$, λ_a 547.9 for 10% solution in benzene; the *inactive* form has m. p. 173°. The corresponding *anisylidene* compound crystallises in large, pearly scales; the *active* form has m. p. 55°, $[\alpha]_D^{20} + 8.62^\circ$, λ_a 547.7 for 10% solution in benzene; the *inactive* form has m. p. 93°. The ketone also condenses with ethyl acetate under the influence of sodium and with ethyl benzoate in the presence of sodamide; active *acetylamlacetone* [*η-methylnonan-βδ-dione*],



is a pale yellow, viscous oil, b. p. 103°/10 mm., D_4^{20} 0.9202, $[\alpha]_D^{20} + 9.80^\circ$, 8.28° in 10% benzene, λ_a 630.0, 579.7 in benzene solution, and forms a pale green copper salt; active *benzoylamlacetone* [*α-phenyl-ξ-methyloctan-αγ-dione*] is a pale yellow, aromatic oil, b. p. 106–107°/0.1 mm., 180°/10 mm., D_4^{20} 1.005, $[\alpha]_D^{20} + 9.41^\circ$, 6.87° in 10% benzene, 6.44° in 10% solution in 10% sodium hydroxide, λ_a 620.0, 580.0 in benzene, 587.7 in sodium hydroxide, and it forms a pale green copper salt.

Some menthyl derivatives were prepared for comparison with these. Menthyl acetoacetate has b. p. 149.5°/10.25 mm., D_4^{20} 0.9866, $[\alpha]_D^{20} - 69.21^\circ$, 69.32° in 10% benzene, λ_a 678.9, 698.7 in benzene. The sodium compound of this reacts with *α*-bromoethylbenzene to form *menthyl α-phenylethylacetoacetate* (*menthyl α-acetyl-β-phenylbutyrate*), $\text{CHMePh}\cdot\text{CHAc}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$, as a thickly matted mass of slender needles, m. p. 98°, b. p. 217°/11 mm., $[\alpha]_D^{20} + 108.16^\circ$, λ_a 635.2, for 10% solution in benzene. [The corresponding *ethyl ester* has b. p. 154°/11 mm.] This may be hydrolysed to *δ-phenylpentan-β-one*, b. p. 109–110°/11 mm. Menthyl sodioacetoacetate also reacts with active amyl bromide to form *menthyl amylacetoacetate*, b. p. 185°/10 mm., D_4^{20} 0.9723, $[\alpha]_D^{20} - 40.48^\circ$, λ_a 698.8.

The rotations for the *C*, *E*, and *F* lines, and the values of $[\alpha]_F/[\alpha]_C$ and $[\alpha]_F - [\alpha]_C$ are also given.

With the exception of the menthyl derivatives, it will be seen that the highest rotatory power is possessed by the active ethyl amylacetoacetate, in which the asymmetric grouping is bounded by two carbonyl groups. With only one carbonyl group, as in amylacetone, the rotatory power is much less, but is still higher than that of amyl alcohol, and the rotation is almost as low if the two carbonyl groups are not near the asymmetric carbon atom, as in the two acylamlacetones. The "characteristic wave-lengths," λ_m , for the pure compounds vary considerably, but the values for the solutions are about the same. Certain constitutional differences must therefore disappear on dissolving the compounds, and the effect of the solvent on the rotation-dispersion is consequently very pronounced.

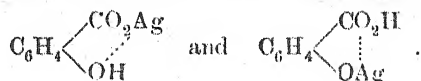
J. C. W.

Some New Compounds of Dextrose. P. KARRER (*Ber.*, 1917, 50, 833–837. Compare *A.*, 1916, i, 832).—By the interaction of bromoacetoglucose and the silver salt of an organic acid in an

inert solvent, tetra-acetyl derivatives of the corresponding ester of dextrose have been obtained. Unfortunately, it has not been found possible to eliminate the acetyl radicles without simultaneously removing the organic acid group, so that the influence of the dextrose molecule on the physiological activity of the acids employed could not be observed.

In boiling toluene, silver 2-phenylquinoline-4-carboxylate and bromoacetoglucose react with the formation of *tetra-acetyl-dextrose* 2-phenylquinoline-4-carboxylate, $\text{N} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CPh}\cdot\text{CH} \end{smallmatrix} \text{CO}_2\cdot\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4$, needles, m. p. 151° , which on treatment with methyl-alcoholic ammonia yields 2-phenylquinoline-4-carboxylamide, $\text{C}_{16}\text{H}_{12}\text{ON}_2$, needles, m. p. 196° .

Under similar conditions, bromoacetoglucose and silver salicylate react, giving rise to two isomeric substances, namely, *tetra-acetyl-dextrose salicylate*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4$, crystals, m. p. 185° , and *salicylic acid tetra-acetylglucoside*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4$, a levorotatory substance, m. p. 167° . The former gives a violet coloration with ferric chloride, and with methyl-alcoholic ammonia yields salicylamide, whereas the latter gives no coloration and is soluble without fission in very dilute aqueous ammonia, whilst on hydrolysis with alkalis or more concentrated ammonia it yields salicylic acid. The formation of these two isomerides is attributed to the co-existence of two modifications of silver salicylate, namely,

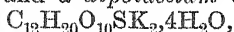


D. F. T.

Synthesis of Disaccharides containing Sulphur and Selenium.

WILHELM SCHNEIDER and FRITZ WREDE (*Ber.*, 1917, 50, 793—804. Compare Schneider and others, *A.*, 1916, i, 791, 792; 1914, i, 669, 977).—The interaction of β -bromoacetylglucose and potassium hydrogen sulphide in alcoholic solution gives rise to an uncrystallisable substance, together with the *octa-acetate*, $\text{C}_{28}\text{H}_{38}\text{O}_{18}\text{S}$, colourless needles, m. p. 174° , $[\alpha]_D^{20} = -38.21^\circ$ in *s*-tetrachloroethane, of a disaccharide containing an atom of sulphur. This product probably owes its formation to the presence of normal potassium sulphide in the alcoholic solution. By treatment with a methyl-alcoholic solution of ammonia (Fischer and Helferich, *A.*, 1914, i, 333), the octa-acetate was convertible into the corresponding thio-disaccharide, $\text{C}_{12}\text{H}_{22}\text{O}_{10}\text{S}$, hexagonal leaflets, m. p. 174° , $[\alpha]_D^{20} = -84.78^\circ$ in water, to which, from its apparent analogy with *isotrehalose* (Fischer and Delbruck, *A.*, 1909, i, 633), is given the name *thioisotrehalose*. Thioisotrehalose is remarkably resistant to hydrolytic agents; it is indifferent to warm aqueous alkalis, whilst mineral acids liberate hydrogen sulphide only slowly even in hot concentrated solution; emulsin, yeast enzyme (Lebedeff, *A.*, 1911, i, 248, 828), trehalase, and myrosin are without action. From the fact that Fehling's solution is not reduced, it is probable that thioisotrehalose does not contain an aldehydic group. Thioisotrehalose

gives a *potassium* derivative, $C_{12}H_{21}O_{10}SK \cdot 2H_2O$, microscopic needles, decomp. at $170-180^\circ$, and a *dipotassium* derivative,



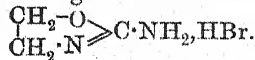
microscopic tetragonal double pyramids, decomp. near 170° .

In a similar way, using an alcoholic solution of potassium selenide, it was possible to obtain an *octa-acetylselenoisotrehalose*, $C_{28}H_{38}O_{18}Se$, colourless needles, m. p. 186° , $[\alpha]_D^{25} -51.24^\circ$ in *s*-tetrachloroethane, which on hydrolysis with methyl-alcoholic ammonia gave *selenoisotrehalose*, $C_{12}H_{22}O_{10}Se$, crystals closely resembling the corresponding thio-compound, m. p. 193° , $[\alpha]_D^{25} -83.58^\circ$ in water; *potassium* derivative, $C_{12}H_{21}O_{10}SeK \cdot 2H_2O$, needles, decomp. near 132° ; *dipotassium* derivative, $C_{12}H_{20}O_{10}SeK_2 \cdot 4H_2O$, tetragonal, double pyramids, decomp. near 130° . Like the thio-analogue, *selenoisotrehalose* is a sweet substance of remarkable resistance to hydrolysis and mild oxidising agents. Not only are these compounds unaffected by the hydrolytic agents mentioned above, but when administered to dogs or guinea-pigs they are eliminated unaltered in the urine.

D. F. T.

Bromoethylamine. S. GABRIEL (*Ber.*, 1917, **50**, 826—827).—Bromoethylamine is prepared most conveniently by saturating at 0° with hydrogen bromide a mixture of aminoethyl alcohol and fuming hydrobromic acid, the resulting mixture being heated for one hour at 170° ; the m. p. of bromoethylamine hydrobromide is $172.5-173.5^\circ$, and not $155-160^\circ$, as stated previously.

When hydroxyethylcarbamide is heated with fuming hydrobromic acid, solution at 100° for one hour the product is unstable *bromoethylcarbamide*, $CH_2Br \cdot CH_2 \cdot NH \cdot CO \cdot NH_2$, needles, m. p. 91° , which on being kept for several days undergoes transformation into ethylene- ψ -carbamide hydrobromide,



D. F. T.

Palladium. A. GUTBIER and C. FELLNER [with J. KRAÜTER, F. FALCO, A. KRELL, FR. SCHULZ, and M. WOERNLE] (*Zeitsch. anorg. Chem.*, 1916, **95**, 129—168. Compare A., 1905, i, 584, 876; 1906, i, 12, 244, 402; ii, 407; 1909, ii, 585; 1910, ii, 459, 756).—The following compounds are described: *tetramethylammonium palladochloride*, $(NMe_4)_2PdCl_4$, dark red, pleochroic crystals; *isopropylammonium palladochloride*, $(NH_3 \cdot C_3H_7)_2PdCl_4$; *n-butylammonium palladochloride*, $(NH_3 \cdot C_4H_9)_2PdCl_4$; *diisobutylammonium palladochloride*, $[NH_2(C_4H_9)_2]_2PdCl_4$; *allylammonium palladochloride*, $(NH_3 \cdot C_3H_5)_2PdCl_4$; and the corresponding mono-, di-, and tri-isocamylammonium, guanidinium, benzylanilinium, o-, m-, and p-chloro- and bromo-anilinium, o-, m-, and p-nitroanilinium, tri-benzylammonium, dimethyl-o-toluidinium, o-, m-, and p-xylydinium, ψ -cumidinium, 2:4-tolylenediammonium, diphenylmethylanmonium, o- and p-phenetidinium, β -picolinium, lutidinium, collidinium, piperidinium, and isoquinolinium palladochlorides.

In the hexachloro-series, *dimethylammonium palladichloride*, $(NH_2Me_2)_2PdCl_6$ is bright red and unstable, and the tri- and tetra-

methylammonium, *di*-, *tri*-, and *tetra-ethylammonium*, *isopropylammonium*, *di*- and *tri-propylammonium*, *n-butylammonium*, *di*- and *tri-isobutylammonium*, *mono*-, *di*-, and *tri-isamylammonium*, β -*picolinium*, *lutidinium*, *collidinium*, and *isoquinolinium palladi-chlorides* are quite similar.

The corresponding bromides of both series have been prepared from most of the same bases.

The following palladodiammine derivatives are described:

isoPropylpalladesammine chloride, $\text{Pd}(\text{NH}_2\cdot\text{C}_3\text{H}_7)_2\text{Cl}_2$; and the corresponding *di-propyl*, *n-butyl*, *di-isobutyl*, *mono*-, and *di-isamyl*, *benzylidenecaniline*, *o*-, *m*-, and *p-nitroaniline*, *o*-, *m*-, and *p-xylylene*, 2:4- and 3:4-*tolylenediamine*, *p-phenetidine*, β -*picoline*, *lutidine*, *collidine*, *piperidine*, and *isoquinoline* compounds. Iodides and bromides of most of the bases have been prepared, as well as the nitrates from *pyridine*, $\text{Pd}(\text{C}_5\text{NH}_5)_2(\text{NO}_3)_2$, and α -*picoline*, $\text{Pd}(\text{C}_5\text{NH}_4\text{Me})_2(\text{NO}_3)_2$. C. H. D.

A New Class of Palladium Compounds. Palladous Trichlorides and Tribromides. A. GUTHRIE and C. FELLNER (*Zeitsch. anorg. Chem.*, 1916, **95**, 169—176).—Whilst palladous compounds with salts of organic amines usually correspond with two subsidiary valencies of the central atom, under certain conditions only one subsidiary valency may be active. This is very unusual, only one example being recorded in the large series of platinous compounds. The formation depends less on the relative proportions of the compounds than on the concentration, low concentrations favouring the trichloride and high concentrations the tetrachloride. Slow crystallisation at atmospheric temperatures is most suitable. The crystals are brown or red.

The *tripropylammonium*, $[\text{NH}(\text{C}_3\text{H}_7)_3][\text{PdCl}_3]$, *di*- and *tri-isobutylammonium*, *guanidinium*, *aminoguanidinium*, and *benzylethylammonium chlorides*, and the *tetra-ethylammonium*, *tripropylammonium*, *collidinium*, and *tribenzylammonium bromides* are described.

C. H. D.

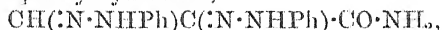
Oxidation of Amino-acids and of Related Substances with Chloramine-T. HENRY DRYSDALE DAKIN (*Biochem. J.*, 1917, **11**, 79—95. Compare A., 1916, i, 598).—In a previous paper (*loc. cit.*) an account has been given of the oxidation of simple amino-acids by the neutral oxidising agent, chloramine-T (sodio-*p*-toluenesulphonchloroamide). The work has now been extended to a study of the behaviour of more complex amino-acids towards the same reagent.

When monosodium glutamate is treated with one molecular proportion of chloramine-T a good yield of the semi-aldehyde of succinic acid, β -aldehydopropionic acid, is obtained. The substance is readily isolated as the nitrophenylhydrazone, which crystallises in platelets, m. p. 185—187° (Alefeld, A., 1909, i, 364, gives 175°). Using two molecules of chloramine-T to one of the glutamate, the reaction takes a different course with formation of β -cyanopropionic acid, $\text{C}_4\text{H}_5\text{O}_2\text{N}$, crystallising in stout prisms, m. p. 48—50°. On

evaporation with concentrated hydrochloric acid, it is converted quantitatively into succinic acid, and by means of sodium and alcohol it is reduced to γ -aminobutyric acid. The latter substance has also been obtained by the bacterial decomposition of glutamic acid.

The oxidation of sodium aspartate by chloramine-T occurs readily in aqueous solution with the liberation of ammonia and carbon dioxide. The chief product isolated is dichloroacetaldehyde, which yields characteristic derivatives of glyoxal when treated with phenylhydrazine or *p*-nitrophenylhydrazine. Methylaspartic acid similarly yields derivatives of methylglyoxal with the intermediate formation of dichloroacetone, whilst *isobutaldehyde* and β -methylbutaldehyde are formed from valine and *isoleucine* respectively.

On oxidising aqueous solutions of asparagine with chloramine-T, a reducing substance is formed which on treatment with phenylhydrazine and other bases gives derivatives of mesoxalic semialdehyde. The substance is not isolated in the pure state, but the derivatives obtained from it indicate that it is probably the semialdehyde of dichloromalonamide, $\text{CHO} \cdot \text{CCl}_2 \cdot \text{CO} \cdot \text{NH}_2$. Dichloroacetamide also occurs among the oxidation products of asparagine. On treating the oxidation products with phenylhydrazine, mesoxamide semialdehydebisphenylhydrazone,



is formed. It crystallises from ethyl acetate in light yellow prisms and needles, m. p. $250-252^\circ$. It is identical with a compound prepared by Langheld (A., 1909, i, 557), erroneously described by him as the phenylhydrazone of the amide of malonic semialdehyde. On boiling with dilute hydrochloric acid, it is converted into 4-benzeneazo-1-phenyl-5-pyrazolone. When *p*-bromophenylhydrazine is substituted for phenylhydrazine in the reaction, *mesoxamide semialdehydebis-p-bromophenylhydrazone*, $\text{C}_{15}\text{H}_{13}\text{O}_5\text{N}_7\text{Br}_2$, is formed. It crystallises in golden-yellow rosettes, m. p. $274-275^\circ$. The corresponding *bis-p-nitrophenylhydrazone*, $\text{C}_{15}\text{H}_{13}\text{O}_5\text{N}_7$, deep red, prismatic needles from nitrobenzene, m. p. about 340° , and *bis-semicarbazone*, $\text{C}_5\text{H}_9\text{O}_3\text{N}_7$, colourless needles, m. p. 240° , were also prepared. A trace of the nitrophenylhydrazone, when treated with sodium hydroxide and alcohol, gives an intense blue solution, a reaction which appears to be characteristic of two adjacent nitrophenylhydrazine groups. By treating the oxidation products of asparagine with 3:4-tolylenediamine, the *amide* of 7-methylquinoxaline-2(or 3)-carboxylic acid, $\text{C}_{10}\text{H}_9\text{O}_3\text{N}_3$, is formed, glistening plates, m. p. $286-287^\circ$.

On heating dextrose with chloramine-T in aqueous solution, oxidation occurs slowly and toluenesulphonamide is precipitated. The addition of phenylhydrazine to the filtrate is followed by the precipitation of a yellow substance, which is found to be the *phenylhydrazone* of *benzaldehyde-p-sulphonamide*, $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}_3\text{S}$, crystallising from alcohol in greenish-gold plates, m. p. $244-245^\circ$ (decomp.). The aldehyde is produced apparently from *p*-toluenesulphonamide by oxidation with unchanged chloramine-T, and can also be prepared directly by heating these two substances together

in aqueous solution. On adding an alcoholic solution of aniline to the solution containing the aldehyde, *benzylidencaniline-p-sulphonamide*, $\text{NH}_2\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH:NPh}$, is precipitated. It is obtained as a felted mass of silky crystals, m. p. 208° . On warming the anil with dilute sulphuric acid, the aldehyde is set free and can be extracted by ether. *Benzaldehyde-p-sulphonamide*, $\text{C}_7\text{H}_7\text{O}_3\text{NS}$, crystallises in shining, colourless plates and needles, m. p. $122\text{--}124^\circ$. It yields a *hydrazone*, $\text{C}_7\text{H}_9\text{O}_2\text{N}_2\text{S}$, shining plates, m. p. $288\text{--}290^\circ$, and a *semi-carbazone*, $\text{C}_8\text{H}_{10}\text{O}_3\text{N}_4\text{S}$, characteristic twin prisms, m. p. $250\text{--}251^\circ$.

H. W. B.

The Origin of the Nitrogenous Pigments in Sugar Refinery Products. VL. STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1917, 41, 607—614. Compare this vol., i, 381, and Stolzenberg, A., 1916, i, 829).—It has been suggested that the nitrogenous pigments (including "fuscazinic acid") in molasses and desaccharification residues may owe their formation to the condensation of amino-acids with sugars during the refinery processes. Maillard (A., 1912, i, 169) has already shown that many free amino-acids react with the common sugars to form such products, but the author has now tested whether such a condensation can take place in more or less alkaline solutions.

It is found that when solutions of invert-sugar or sucrose are heated in an autoclave at $105\text{--}130^\circ$ with sodium glutamate or aspartate, or with asparagine, carbon dioxide is liberated, the solutions become acidic, and dark pigments are formed which are almost completely precipitated by lead acetate. The same pigments are obtained if precipitated chalk is added to overcome the acidity. Without the amino-acid, the colour of the solution is not so deep, and the pigment is completely soluble in alcohol. With the amino-acid, nitrogenous substances which do not dissolve in alcohol are produced as well. A fraction, which somewhat resembles fuscazinic acid in being a very dark brown powder, soluble only in alkalis, has been isolated. Asparagine and aspartic acid give rise to much more of this product than glutamic acid.

J. C. W.

The Nitrogenous Pigments of Molasses. H. FRIEDRICH (*Zeitsch. Zuckerind. Böhm.*, 1917, 41, 614—617).—The author claims that he has been engaged since 1914 on a method for the recovery of the various ingredients in molasses and on a study of the nitrogenous pigments. About 72% of the sucrose can be precipitated in a pure white condition by mixing the molasses with an equal quantity of cold glacial acetic acid. Most of this acid may be recovered in a concentration of 71% by distillation, when a dark brown, asphalt-like mass is left containing about 18% of ash (23.75% K). This residue may be worked up for betaine by trituration with about six times its bulk of methyl alcohol. The insoluble portion (27%) is a nitrogenous pigment containing about 3.4% of nitrogen, and yielding yellow derivatives on nitration.

The author agrees with Staněk (see preceding abstract) as to

the nature of the nitrogenous pigment, except that he regards the condensation of the amino-acids as taking place with caramel substances rather than with the sugars themselves. He therefore proposes the term "caramelazine substances." J. C. W.

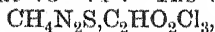
The Nitrogenous Pigments of Molasses. VL. STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1917, **41**, 618).—A reply to Friedrich (preceding abstract). He points out that the pigments which he has obtained by heating solutions of sugars and salts of amino-acids were formed at temperatures below that at which caramel is produced. He also suggests that Friedrich is dealing, not only with the original pigments of molasses, but also with new ones produced during the distillation by the condensation of the invert-sugar and amino-acids under the influence of the acetic acid.

J. C. W.

Condensation Product of Ammonium Thiocyanate with Formaldehyde. SCHMERDA (*Zeitsch. angew. Chem.*, 1917, **30**, i, 176).—In concentrated aqueous solution, ammonium thiocyanate combines directly with formaldehyde; 1 mol. or more of formaldehyde unites with 1 mol. of thiocyanate. The product is only sparingly soluble in water or ordinary solvents, and is decomposed by strong acids or alkalis.

W. P. S.

Salts of Thiocarbamide. AUGUSTUS EDWARD DIXON (T., 1917, **111**, 684—690).—Since the solubility of thiocarbamide in water is increased by the presence of strong acids, it appears that salts are formed in these solutions, but these are markedly hydrolysed and their isolation is difficult. The hydrochloride (Stevens, T., 1902, **81**, 80) is now found to dissolve to the extent of 1.48 parts to 6.65 parts of water. It has the formula $\text{CH}_4\text{N}_2\text{S}\cdot\text{HCl}$, m. p. 136—137°. A salt with 2HCl was not detected. With sulphuric acid, the salt isolated has the formula $\text{CH}_4\text{N}_2\text{S}\cdot\text{H}_2\text{SO}_4$, and is a white, crystalline, hygroscopic substance. The nitrate (Emerson Reynolds, this Journ., 1869, **22**, 5) is soluble, for 1 part of thiocarbamide, in about 6.5 parts of water. The oxalate, $\text{CH}_4\text{N}_2\text{S}\cdot\text{H}_2\text{C}_2\text{O}_4$, melts at 73—74°. The trichloroacetate,



and the picrate, $\text{CH}_4\text{N}_2\text{S}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, were also prepared. The constitution of these salts is briefly discussed.

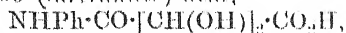
T. S. PA.

Amides and Imides of Tartaric Acid. I. L. CASALE (*Gazzetta*, 1917, **47**, i, 272—285).—*d*-Tartaric acid forms with aniline two salts, namely, aniline hydrogen *d*-tartrate and aniline *d*-tartrate, $[\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}\cdot\text{NH}_2\text{Ph}]_2 + 4\text{H}_2\text{O}$ (Hilditch, T., 1911, **99**, 224, gave $3\text{H}_2\text{O}$), which lose water of constitution when heated, yielding the corresponding imide and amide respectively. Phenyltartramide readily takes up: (1) 1 mol. of water, to form an amic acid; (2) 1 mol. of alcohol, to form an ester of such amic acid; and (3) 1 mol. of ammonia or of an amine, to form a diamide. The chemical behaviour of phenyltartramide pointed to a lactic

constitution, but such a conclusion is excluded by the results of a molecular weight determination in acetone.

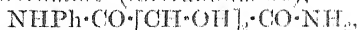
d-Phenyltartramide (tartranil) forms nacreous leaflets with straw-coloured reflection, m. p. 255° (corr.; decomp.). Its solubility in cold water is very slight, and cannot be determined owing to the transformation of the compound into tartranilic acid. The value given by Frankland and Slator (T., 1903, **83**, 1319) for the specific rotation of *d*-phenyltartramide in an aqueous solution containing 0.5964 gram per 100 grams of the solvent is invalid, such concentration being unattainable with the pure compound; it has the normal molecular weight in boiling acetone, and its specific rotation in methyl alcohol is $[\alpha]_D^{15} + 130^\circ$.

d-Phenyltartramic (tartranilic) acid,



forms white, silky needles, m. p. 194° (corr.), and behaves as a weak monobasic acid; in aqueous solution, the value of $[\alpha]_D^{15}$ is +105.6°—106.8°, and in methyl alcohol, +114.7°. When heated, the acid yields tartranil, m. p. 255° (corr.), and an isomeride of the latter, m. p. 262° (corr.). The following salts of tartranilic acid were prepared: *sodium*, m. p. 226° (corr.), $[\alpha]_D^{15} + 141.25^\circ$; *ammonium*, $[\alpha]_D^{15} + 102.2^\circ$; *silver*; *methyl*, colourless needles, m. p. 175° (corr.), $[\alpha]_D^{15} + 106^\circ$; *ethyl*, prismatic needles, m. p. 163° (corr.), $[\alpha]_D^{15} + 102.4^\circ$; *propyl*, m. p. 161° (corr.), $[\alpha]_D^{15} + 99.1^\circ$; *isobutyl*, m. p. 158° (corr.), $[\alpha]_D^{15} + 92.6^\circ$; *isoamyl*, m. p. 135° (corr.), $[\alpha]_D^{15} + 89.2^\circ$.

d-Monophenyltartramide (tartranilamide),



prepared by dissolving phenyltartramide in hot concentrated ammonia solution, forms shining, white leaflets, m. p. 226° (corr.), $[\alpha]_D^{15} + 139^\circ$ in water or +153° in methyl alcohol. T. H. P.

Action of Sodium Hypochlorite on Amides of α -Hydroxy-acids and of Polyhydroxy-acids having a Hydroxyl Group in the α -Position. A New Method for the Degradation of Sugars. R. A. WEERMAN (*Rec. trav. chim.*, 1917, **37**, 16—51).—

A more detailed account and an extension of work already published (compare A., 1915, i, 387). Among the products of the addition of hydrazine sulphate to a mixture of mandelamide and sodium hypochlorite in methyl alcohol, azodicarbonamide was given instead of hydrazodicarbonamide.

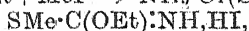
By the method described (*loc. cit.*), *l*-mannose was converted through *l*-mannonamide into *l*-arabinose, and *l*-arabinose through *l*-arabonamide, m. p. 132—133° (decomp.), $[\alpha]_D^{14} + 38.4^\circ$, into *l*-erythrose, isolated as its phenylbenzylhydrazone. Attempts to carry out the degradation of *l*-gulose, *l*-ribose, *l*-xylose, *isosaccharinamide*, and phenylglyceramide were not successful, owing to the instability or the poor yields of the necessary amides.

The author has obtained tartramic acid in a crystalline form, m. p. 171—172°, $[\alpha]_D^{15} + 63.7^\circ$, and the crystallographic measurements confirm those of Pasteur (*Ann. Chim. Phys.*, 1853, [iii], **38**, 454).

The action of sodium hypochlorite on the amides of hydroxy-acids furnishes a ready means of showing whether there is a hydroxyl group in the α -position. If to the reaction mixture semicarbazide is added and hydrazodicarbonamide is formed, the presence of a hydroxyl group in the α -position is indicated. W. G.

Imino-esters. III. The Constitution of Salts of the Imino-esters. ANGELO KNORR (*Ber.*, 1917, 50, 767—772).—The conversion of the esters of thioncarbamic acid, $\text{NH}_2\cdot\text{CS}\cdot\text{OR}$, into the corresponding thiolcarbamates, $\text{NH}_2\cdot\text{CO}\cdot\text{SR}$, under the influence of alkyl haloids, has been attributed to the intermediate formation of an additive compound of the thioncarbamate and the alkyl haloid, the subsequent re-elimination of the haloid giving rise to the thiolcarbamate (Wheeler and Barnes, A., 1899, i, 797). The author has now found that an additive compound of this type actually is formed in the action of methyl iodide on ethyl thioncarbamate (xanthogenamide), but that the constitution of this product is that of a *hydriodide of ethyl iminomethylthiolcarbonate*, $\text{SMe}\cdot\text{C}(\text{OEt})\cdot\text{NH}_2\cdot\text{HI}$; this forms needles, m. p. 58—60°, decomposing into ethyl iodide and methyl thiolcarbamate, $\text{NH}_2\cdot\text{CO}\cdot\text{SMe}$; its constitution was further demonstrated by conversion into the corresponding hydrochloride by successive treatment with potassium carbonate solution and ethereal hydrogen chloride and also into the *acetyl* derivative, $\text{SMe}\cdot\text{CO}\cdot\text{NHAc}$, prisms, m. p. 144°, by the action of acetic anhydride; the analogous *acetyl* derivative of ethyl thiolcarbamate, $\text{SEt}\cdot\text{CO}\cdot\text{NHAc}$, prisms, m. p. 97—98°, was obtained by the action of acetic anhydride on ethyl iminoethylthiolcarbonate or on the hydrochloride of this compound.

For the explanation of this transformation the author suggests the stages $\text{NH}_2\cdot\text{CS}\cdot\text{OEt} + \text{MeI} \rightarrow \text{NH}_2\cdot\text{CI}(\text{SMe})\cdot\text{OEt} \rightarrow$



the intermediate carbonium salt occurring only transiently (compare Wheeler and Barnes, *loc. cit.*; Billmann, A., 1909, i, 143). The results of the investigation confirm Pinner's views as to the constitution of the salts of the imino-esters. D. F. T.

Crystallography of some Compounds of Glutamic Acid and Glutiminic Acid. L. KAPLANOVA (*Abh. Böhm Akad.*, 1915, No. 23, 8 pp.; from *Jahrb. Min.*, 1917, i, 123—124).—An interesting example of pseudoracemism and racemism with morphotropy is given by the following group of salts of glutamic acid:

	Active.	Inactive.
Hydrochloride.....	{ Rhombic, 0.8852 : 1 : 0.3866 D 1.525	{ Ditto D 1.525
Hydrobromide.....	{ Rhombic, 0.8784 : 1 : 0.4033 D 1.790	{ Ditto D 1.814
Hydriodide	{ Rhombic, 0.8835 : 1 : 0.4318 D 1.982	{ Triclinic D 2.030

The interfacial angles of the triclinic inactive hydriodide approach the corresponding angles of the active rhombic crystals. The

optical orientation and cleavage are identical in the hydrochlorides and hydrobromides, but differ somewhat in the hydriodides.

L. J. S.

Electrolytic Diazotisation of an Aliphatic Compound.

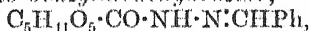
ROBERT B. KRAUSS (*J. Amer. Chem. Soc.*, 1917, **39**, 1427—1431).—When a current of 3·5 amperes at 7 volts is run for about four hours through a cell comprising a copper cooling coil as cathode in 30% sodium hydroxide, and a rotating platinum gauze anode in a solution of glutamic acid (30), sodium nitrite (30), and sodium hydroxide (34), there is every indication of the production of the *iso*-diazotate. The anolyte becomes orange-yellow, and from it a creamy solid may be isolated, which yields a *p*-chlorobenzoyl derivative, m. p. 191°, and a β -naphthalenesulphonyl compound, m. p. 185—186°, and gives typical dyes on coupling with aromatic bases. It is hoped that the compound may soon be obtained pure enough for a thorough characterisation.

J. C. W.

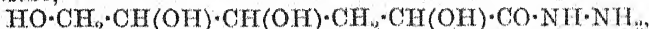
The Hydrazides of Acids Produced by the Oxidation of Sugars.

R. A. WEERMAN (*Rec. trav. chim.*, 1917, **37**, 52—66).—In an endeavour to find a method for the degradation of sugars without the accompanying formation of metallic salts, the hydrazides of the acids arising from the oxidation of certain sugars have been prepared, but are not suitable for the object in view. These hydrazides readily give condensation products with benzaldehyde.

D-Gluconolactone when boiled in alcoholic solution with hydrazine hydrate gives *d*-gluconic hydrazide, m. p. 142—144° (decomp.), $[\alpha]_D^{16} + 30\cdot6^\circ$, which with nitrous acid gives *s*-digluconic hydrazide, $C_{12}H_{24}O_{12}N_2\cdot H_2O$, m. p. 178—179°, $[\alpha]_D^{19} + 66\cdot4^\circ$, and with benzaldehyde gives *d*-gluconic benzylidenhydrazide,



m. p. 157—158°. 1-Mannonic hydrazide, m. p. 161—162°, $[\alpha]_D^{15} + 4\cdot4^\circ$, gives a benzylidenhydrazide, m. p. 194—195°. 1-Arabinonic hydrazide has m. p. 138—139°, $[\alpha]_D^{15} + 51\cdot9^\circ$. *m*-Saccharinic hydrazide,



m. p. 122—123°, $[\alpha]_D^{15} + 18\cdot1^\circ$, behaves somewhat differently from the other hydrazides in that carbon dioxide is among the products of its decomposition with nitrous acid.

W. G.

The Crystalline Form of Diphenyliodonium Chloride,

$C_{12}H_{10}I\cdot Cl$. A. L. W. E. VAN DER VEEN (*Zeitsch. Kryst. Min.*, 1916, **55**, 372—373).—The crystals are monoclinic sphenoidal $[a:b:c = 1\cdot2195:1:1\cdot1871; \beta = 102^\circ 15']$. They were grown from aqueous solution, and it is noteworthy that all were of the left-handed type, no crystals of the enantiomorphous type being obtained. Cleavage on {100} perfect. The optic axial plane is {010}. $D_{20} 1\cdot67 \pm 0\cdot005$.

E. H. R.

Crystallographic Investigation of some Nitro-derivatives of Benzene. H. STEINMETZ (*Zeitsch. Kryst. Min.*, 1915, **54**, 467—497).—*m*-Dinitrobenzene forms rhombic, bipyramidal crystals

[$a:b:c=0.9435:1:0.5434$]; cleavage {100}; D 1.570; M.V. 107.01.

o-Chloronitrobenzene and *o*-bromonitrobenzene crystallise in the monoclinic system, whilst *o*-iodonitrobenzene is rhombic. Owing to paucity of forms developed, neither could be measured completely.

m-Chloronitrobenzene crystallises in the pyramidal class of the rhombic system, the crystals being markedly hemimorphic [$a:b:c=0.5604:1:0.5004$]. Cleavage {010} perfect; {100} poor. D¹⁵ 1.582; M.V. 99.56.

m-Bromonitrobenzene is isomorphous with the last [$a:b:c=0.5490:1:0.4928$]; D 1.969; M.V. 102.59.

m-Iodonitrobenzene forms monoclinic crystals [$a:b:c=2.2920:1:2.2581$; $\beta=104^{\circ}14'$]. It is, however, pseudorhombic, and when the axial ratios are put into the rhombic form, a close, morphotropic relationship to the two preceding compounds becomes apparent. Cleavage {100} perfect, {001} poor; D 2.227; M.V. 111.81.

p-Chloronitrobenzene is monoclinic [$a:b:c=1.9661:1:1.1265$; $\beta=97^{\circ}21'$]. Cleavage poor, {100} and {110}. D 1.520; M.V. 103.62.

p-Bromo- and *p*-iodo-nitrobenzene are isomorphous, forming triclinic crystals. There is little evidence of isodimorphism with the *p*-chloro-compound.

The three following compounds are closely isomorphous:

3:5-Dichloro-1-nitrobenzene, monoclinic [$a:b:c=0.6017:1:0.2847$; $\beta=121^{\circ}20'$]; cleavage {010} perfect; {100} and {001} poor; D 1.712; M.V. 112.15.

3-Chloro-5-bromo-1-nitrobenzene [$a:b:c=0.5902:1:0.2850$; $\beta=122^{\circ}37'$]; D 2.048; M.V. 115.48.

3:5-Dibromo-1-nitrobenzene [$a:b:c=0.5795:1:0.2839$; $\beta=123^{\circ}48'$]; D 2.363; M.V.=118.91.

o-Nitrophenol forms monoclinic crystals [$a:b:c=0.8932:1:0.4769$; $\beta=103^{\circ}34'$]. Cleavage {010}. D 1.495; M.V. 92.98.

m-Nitrophenol, monoclinic [$a:b:c=0.9223:1:0.15(26)$; $\beta=120^{\circ}21'$]. Cleavage {110} perfect, {120} less perfect. D 1.492; M.V. 93.16.

2:6-Dinitrophenol is rhombic bipyramidal [$a:b:c=0.9510:1:0.7449$]. The density of the crystals varied between 1.645 and 1.724. The latter value gives M.V. 111.86.

3:4-Dinitrophenol forms triclinic crystals, D 1.672; M.V. 110.05.

2:3-Dinitrophenol, monoclinic [$a:b:c=1.6133:1:0.9525$; $\beta=111^{\circ}27\frac{1}{2}'$]; D 1.681; M.V. 109.46. Cleavage {001}.

3:5-Dinitrophenol, monoclinic [$a:b:c=0.6816:1:0.3313$; $\beta=100^{\circ}4'$]; cleavage {001}; D²⁰ 1.702; M.V. 108.11. E. H. R.

The Crystalline Form of some Benzene Derivatives.

E. REPOSSI (*Rend. R. Ist. Lomb. sci. lett.*, 1912, (ii^a), 45, 242—271; from *Zeitsch. Kryst. Min.*, 1915, 55, 281—288).—The author has examined the crystalline form of ten of the possible

3:4:5-trihalogen derivatives of nitrobenzene. The six possible compounds containing chlorine and bromine form an isomorphous triclinic series. In addition, 3:5-dichloro-4-bromonitrobenzene exists in a β -monoclinic modification, which is structurally similar to, though not truly isomorphous with, the monoclinic series of compounds containing iodine, of which four have been examined.

3:4:5-Trichloro-1-nitrobenzene, triclinic, tabular crystals from ethyl acetate, m. p. 72.5° [$a:b:c=1.1855:1.04420$; $\alpha=103^\circ11\frac{1}{2}'$; $\beta=91^\circ23'$; $\gamma=77^\circ32'$]. D 1.807 ; M.V. 125.3 . The axial ratios of the other triclinic compounds are similar.

3:4-Dichloro-5-bromo-1-nitrobenzene, bright greenish-yellow, triclinic crystals from a mixture of alcohol and ether; m. p. 82.4° . D 2.074 ; M.V. 130.63 .

3:5-Dichloro-4-bromo-1-nitrobenzene, tabular, sulphur-yellow, triclinic (α -modification) crystals from ethyl acetate; m. p. 88° . D 2.077 ; M.V. 130.44 .

The β -modification forms monoclinic prisms or tables from ethyl acetate or a mixture of this with alcohol and benzene [$a:b:c=0.9227:1.10166$; $\beta=92^\circ14'$]. D 2.079 ; M.V. 130.3 . The crystals become cloudy after a time.

5-Chloro-3:4-dibromo-1-nitrobenzene, greenish-yellow, triclinic tables from a mixture of alcohol and ether; m. p. 97.2° . D 2.376 ; M.V. 132.75 .

4-Chloro-3:5-dibromo-1-nitrobenzene, bright greenish-yellow, triclinic crystals, rich in faces, from mixed solvents, such as benzene, alcohol, and ethyl acetate; m. p. 92° . D 2.397 ; M.V. 131.59 .

3:4:5-Tribromo-1-nitrobenzene, bright yellow, prismatic, triclinic crystals from the usual solvents; m. p. 112° . D 2.645 ; M.V. 138.37 .

3:4:5-Tri-iodo-1-nitrobenzene, sulphur-yellow, monoclinic prisms from chloroform, m. p. 167° [$a:b:c=0.8276:1.09646$; $\beta=90^\circ5'$]. The crystals are plastic at the ordinary temperature and under slight pressure form twins, $\{102\}$ being a gliding plane and also a cleavage plane. D 3.265 ; M.V. 133.35 .

5-Chloro-3:4-di-iodo-1-nitrobenzene, orange-yellow crystals, monoclinic prisms, from chloroform; m. p. 146.5° [$a:b:c=0.9143:1.09936$; $\beta=92^\circ4'$].

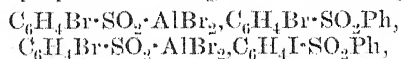
4-Chloro-3:5-di-iodo-1-nitrobenzene, monoclinic prisms from ethyl acetate; m. p. 110° [$a:b:c=0.8137:1.09748$; $\beta=90^\circ38'$]. D 2.827 ; M.V. 144.75 .

5-Bromo-3:4-di-iodo-1-nitrobenzene, imperfect, sulphur-yellow, monoclinic prisms from chloroform; m. p. 146.5° [$a:b:c=0.8184:1.09350$; $\beta=91^\circ34'$]. D 3.085 ; M.V. 147.1 . E. H. R.

Some Derivatives of Benzenesulphinic Acid. S. C. J. OLIVIER (*Rec. trav. chim.*, 1917, **37**, 92—95).—The compound $C_6H_4Br \cdot SO_2 \cdot AlBr_3$, obtained by the action of aluminium bromide on *p*-bromobenzenesulphonyl bromide in solution in carbon disulphide, behaves like aluminium bromide in that it will give additive compounds with certain aromatic sulphones.

If diphenylsulphone is dissolved in dry benzene and aluminium

bromide is added, a clear solution results, from which on the addition of *p*-bromobenzenesulphonyl bromide a viscous liquid separates out, which is the compound $C_6H_4Br \cdot SO_2 \cdot AlBr_2 \cdot SO_2Ph_2$. When this compound is decomposed by water, *p*-bromobenzenesulphinic acid and the sulphone are obtained. Three other such compounds were similarly prepared having the following compositions:



and $C_6H_4Br \cdot SO_2 \cdot AlBr_2 \cdot C_6H_4Me \cdot SO_2Ph$. All these compounds had properties similar to those of the first. W. G.

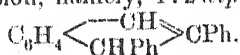
Triphenylmethyl. XXVII. Molecular Weights of the Triarylmethyls. M. GOMBERG and C. S. SCHOEPELE (*J. Amer. Chem. Soc.*, 1917, **39**, 1652—1674).—Triphenylmethyl, diphenyl- α -naphthylmethyl, phenylxanthyl, *p*-tolylxanthyl, *p*-chlorophenylxanthyl, α -naphthylxanthyl, and phenylpheno- β -naphthaxanthyl have been prepared in a pure condition and their molecular weights determined in freezing naphthalene over a fairly wide range of concentration. Under the conditions used, diphenyl- α -naphthylmethyl and α -naphthylxanthyl are entirely unimolecular.

In all cases, the molecular weight increases gradually as the concentration increases from 1% to 6%, molecular dissociation being thus indicated. When in triphenylmethyl two phenyl groups become joined through an oxygen atom, and thus give rise to a xanthone ring, the tendency to dissociate is markedly increased. A phenyl and a *p*-tolyl group are apparently equivalent in their influence for dissociation when linked to a xanthone ring, whereas the influence of a *p*-chlorophenyl group is somewhat less. An α -naphthyl group when replacing a phenyl group in triphenylmethyl exerts on the dissociation equilibrium of the compound a decided influence in favour of the unimolecular phase, diphenyl- α -naphthylmethyl being wholly dissociated. This influence is retained when the naphthyl group is linked to a xanthone ring, the resulting compound being also completely dissociated. When, however, the naphthyl group enters as a component in the formation of the xanthone ring itself, it causes a considerable lowering of the tendency of the compound to dissociate.

The triarylmethyls are almost wholly devoid of colour in the solid state, whereas their solutions are yellow, orange, brown, red, or green, the coloration being regarded as due to tautomerisation of the compounds into their quinonoid modifications. T. H. P.

1:2- and 2:3-Diphenylindene. PAUL RUGGLI (*Annalen*, 1917, **414**, 125—130).—By the addition of bromine to $\alpha\beta\gamma$ -triphenylpropene, and subsequent elimination of hydrogen bromide, Orzechoff (A., 1914, i, 265) obtained a hydrocarbon, m. p. 178°, which he designated 2:3-diphenylindene. A compound, m. p. 108°, which must have this constitution, was previously obtained from benzylidenedecoxybenzoin by Thiele and Ruggli (A., 1912,

i, 866). It is now shown that Orechhoff's compound was the other alternative of his reaction, namely, 1:2-diphenylindene,



Orechhoff's objection to this formula was that the hydrocarbon condensed with benzaldehyde to form 2:3-diphenyl-1-benzylideneindene, but this is explained by the fact that 1:2-diphenylindene undergoes rearrangement into the 2:3-compound, which yields the same condensation product, in the presence of potassium hydroxide.

J. C. W.

I-Phenanthrene-10:3 (or 6)-disulphonic Acid. HÅKAN SANDQVIST (*Ber.*, 1917, 50, 774—777).—The author provisionally distinguishes between the two isomeric 10-bromophenanthrene-3- or -6-sulphonic acids (*A.*, 1915, i, 795; 1916, i, 206; ii, 556) by the prefixes I and II. The I-isomeride slowly reacts with aqueous sodium sulphite solution at 260—270°, with the formation of the easily soluble sodium salt (needles) of I-phenanthrene-10:3(or 6)-disulphonic acid, $\text{C}_{14}\text{H}_8(\text{SO}_3\text{H})_2 \cdot 4\text{H}_2\text{O}$, needles, m. p. 157° with rapid heating, or when anhydrous, m. p. 233° (decomp.); barium salt, rhombic crystals with $2\frac{1}{2}\text{H}_2\text{O}$. The corresponding acid chloride, $\text{C}_{14}\text{H}_8\text{O}_4\text{Cl}_2\text{S}_2$, prepared by the action of phosphorus pentachloride on the sodium salt, forms yellow prisms, which melt at 220—221° with liberation of sulphur dioxide and a little hydrogen chloride, and with the formation of a substance, m. p. 196—197°, probably I-10-chlorophenanthrene-3(or 6)-sulphonic acid.

The disulphonic acid does not resemble the I-10-bromo-3(or 6)-sulphonic acid in the characteristic behaviour of the aqueous solutions of the latter with respect to viscosity and anisotropy.

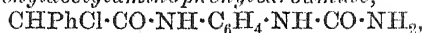
D. F. T.

Methods for the Acylation of Aromatic Amino-compounds and Carbamides, with especial Reference to Chloroacetylation. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1917, 39, 1439—1447).—Chloroacetyl-, benzoyl-, and α -chlorophenylacetyl derivatives of amines are very conveniently prepared by adding a slight excess of the acyl chloride to a chilled solution of the base in a mixture of equal parts of glacial acetic acid and concentrated sodium acetate solution. The products usually crystallise out as formed. Chloroacetylation of carbamides is best performed by dissolving or suspending the compounds in molten chloroacetic acid and then adding the chloride.

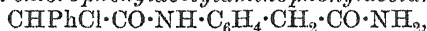
The following compounds have been prepared by these methods: α -Chloroacetanilide, m. p. 136—137°; chloroaceto-piidoanilide^d, $\text{C}_6\text{H}_4\text{I}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, m. p. 191—194°; m-chloroacetylaminophenol^d (*A.*, 1915, i, 671); p-chloroacetylaminophenol, rosettes of glistenin^d platelets, m. p. 144·5—146° (corr.); o-chloroacetylaminobenzamide^{an}, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$, silky hairs, m. p. 183—184·5°; m-chloroacetylaminobenzamide, aggregates of minute crystals, m. p. 215°, which forms a hexamethylenetetraminium salt, $\text{C}_{15}\text{H}_{21}\text{O}_2\text{N}_6\text{Clun}$

m. p. 169—170° (decomp.); *m*-chloroacetylaminobenzoic acid, m. p. 230—232° (decomp.); *p*-chloroacetylaminobenzamide, silky needles, m. p. 241—243° (decomp.); *p*-aminophenylacetamide, scales, m. p. 161—162° (corr.); *p*-chloroacetylaminophenylacetamide, thin, rectangular plates, m. p. 191—191.5° (corr.).

p- α -Chlorophenylacetylaminophenylcarbamide,



crystallises in minute platelets and needles, m. p. 200—201° (decomp.); *m*- α -chlorophenylacetylaminophenol, forms aggregates of spindles, m. p. 157—158° (decomp.); *m*- α -chlorophenylacetylaminobenzamide, separates in minute platelets, m. p. 218° (decomp.); *p*- α -chlorophenylacetylaminophenylacetamide,



forms thin plates and needles, m. p. 184.5—185.5°.

o-Carbamidophenol is benzoylated in pyridine solution and the product, *o*-carbamidophenyl benzoate, aggregates of minute spears, m. p. 178—179° (corr.), converted by the method indicated above into *o*-chloroacetylcarbamidophenyl benzoate,



voluminous rosettes of silky hairs, m. p. 219° (decomp.). Similarly, *m*-carbamidophenyl benzoate, lenticular plates, m. p. 183—184° (corr.), yields *m*-chloroacetylcarbamidophenyl benzoate, in rosettes of long, flat needles, m. p. 188—189.5°. J. C. W.

The Crystalline Form of some Benzene Derivatives. E.

ARTINI (*Rend. R. Ist. Lomb. sci. lett.*, 1912, (ii), 45, 632—644; from *Zeitsch. Kryst. Min.*, 1915, 55, 288—291).—Crystals of the six possible 2:6-dihalogen derivatives of *p*-nitrodiacetanilide have been examined. The dichloro-, chlorobromo-, and chloriodo-compounds form a monoclinic isomorphous series, whilst the dibromo-compound is symmorphous with these, but is triclinic. The bromiodo- and di-iodo-compounds form a distinct triclinic group.

2:6-Dichloro-4-nitrodiacetanilide [$a:b:c=1.1361:1.0:0.8753$; $\beta=70^\circ 4'$]. M. p. 142—143°. D 1.565; M.V. 185.98.

2-Chloro-6-bromo-4-nitrodiacetanilide [$a:b:c=1.1127:1.0:0.8509$; $\beta=70^\circ 36'$]. M. p. 139°. D 1.749; M.V. 191.86.

2-Chloro-6-iodo-4-nitrodiacetanilide [$a:b:c=1.038:1.0:0.799$; $\beta=108^\circ 16'$]. M. p. 113°. D 1.913; M.V. 199.93.

2:6-Dibromo-4-nitrodiacetanilide [$a:b:c=1.0901:1.0:0.8325$; $\alpha=88^\circ 43'$; $\beta=109^\circ 10'$; $\gamma=86^\circ 34'$]. D 1.939; M.V. 196.02.

2-Bromo-6-iodo-4-nitrodiacetanilide [$a:b:c=0.9470:1.0:0.7288$; $\alpha=96^\circ 1'$; $\beta=102^\circ 33'$; $\gamma=80^\circ 53'$]. M. p. 134°; D 2.112; M.V. 202.16.

2:6-Di-iodo-4-nitrodiacetanilide [$a:b:c=0.9682:1.0:0.7260$; $\alpha=83^\circ 7'$; $\beta=76^\circ 8\frac{1}{2}'$; $\gamma=99^\circ 43'$]. M. p. 170—171°; D 2.290; M.V. 206.93. E. H. R.

The Different Methods of Decomposition of Amines by Catalysis: Regeneration of Aniline from Substituted Anilines. PAUL SABATIER and G. GAUDION (*Compt. rend.*, 1917, 165, 309—313).—When the vapour of methylaniline is passed over

reduced nickel at 350° , there is an evolution of ammonia and methane, but the principal product is aniline. The first reaction is $\text{NHPhMe} = \text{NH}_2\text{Ph} + \text{CH}_4$. The methylene groups are decomposed into carbon and hydrogen, which then gives rise to the reaction $\text{NHPhMe} + 2\text{H}_2 = \text{C}_6\text{H}_6 + \text{NH}_3 + \text{CH}_4$. This reaction is, however, of minor importance, the principal change being $2\text{NHMePh} \cdot \text{C} = \text{CH}_4 + 2\text{NH}_2\text{Ph}$. Dimethylaniline similarly gives aniline, carbon, and methane. Ethylaniline is decomposed according to the equation $\text{NHEtPh} = \text{NH}_2\text{Ph} + \text{C}_2\text{H}_4$. The ethylene is immediately decomposed by the nickel, giving carbon and a mixture of methane, ethane, and hydrogen. Diethylaniline behaves similarly. W. G.

Trinitrophenylmethylnitramine (Tetranitromethylaniline). C. F. VAN DUIN (*Rec. trav. chim.*, 1917, **37**, 111—117).—For the safe preparation of trinitrophenylmethylnitroamine in quantity and in order to obtain a good yield, the author considers it necessary to modify Langenscheidt's process (compare A., 1913, i, 457). One hundred grams of dimethylaniline are dissolved in 1 kilogram of sulphuric acid, the temperature being kept below 25° . This solution is poured drop by drop into 500 c.c. of nitric acid (D 1.49), the temperature being kept between 38° and 42° during this process and for three hours after. The temperature is then slowly raised to 50° for half an hour and finally to 55° for two hours. The mixture is allowed to cool and the next day is filtered on glass-wool and washed free from acid with water and then once with alcohol. The substance thus prepared is very stable. It is only very slowly decomposed when boiled with water, giving picric acid.

[With B. C. ROETERS VAN LENNEP.]—The authors consider that the temperature given by Flürscheim and Simon (P., 1910, **26**, 81) for the preparation of tetranitroaniline is too high, and that the temperature during this process should not exceed 50° , the mixture being allowed to remain one day between two heatings for two hours at 50° . After two months, tetranitroaniline commences to decompose, nitrous acid being evolved. W. G.

Some 2:6-Dinitrobenzyl Derivatives. S. REICH and A. OGANESSIAN (*Bull. Soc. chim.*, 1917, [iv], **21**, 117—120).—2:6-Dinitrotoluene is best brominated in the side-chain by heating it in a sealed tube with bromine and magnesium carbonate (compare Rheinhold, "Thesis," Grenoble, 1914). The 2:6-dinitrobenzyl bromide thus obtained gives, with potassium iodide, 2:6-dinitrobenzyl iodide, m. p. 100° — 101° . With a concentrated aqueous solution of potassium cyanide an alcoholic solution of the bromide gives 2:6-dinitrophenylacetonitrile, yellowish-brown crystals, m. p. 202° . If a benzene solution of 2:6-dinitrobenzyl bromide is saturated with ammonia, 2:6:2':6'-tetranitrodibenzylamine, pale yellow needles, m. p. 194° , is obtained, giving a sulphate, m. p. 235° ; a hydrobromide, m. p. 202° ; a platinichloride, m. p. 236° ; a nitrosoamine, m. p. 173° ; and an acetyl derivative, m. p. 189° . When a molecular mixture of dinitrobenzyl bromide and potassium phthalimide is heated for three hours at 130° — 135° it yields 2:6-dinitrobenzyl-

phthalimide, m. p. 178° , which, when heated with fuming hydrochloric acid in a sealed tube at 170 – 180° for six hours, yields *2:6-dinitrobenzylamine*, brown needles, m. p. 88° , giving a *hydrochloride*, m. p. 185° , and a *platinichloride*, m. p. 193° . W. G.

A Series of Four Primary Amines, having the Amino group Linked to a Tertiary Carbon Atom, and some of their Derivatives. M. BRANDER (*Rec. trav. chim.*, 1917, 37, 67–87).—The four amines, *tert*-butylamine, α -phenylisopropylamine, $\alpha\alpha$ -diphenylethylamine, and triphenylmethylamine, have been prepared, and their behaviour towards certain reagents studied. They can all be prepared by the action of ammonia on the corresponding alkyl chloride. The first amine was only obtained in very small amount, but a much larger yield of the second was obtained. $\alpha\alpha$ -Diphenylethylamine, $\text{CMePh}_2\cdot\text{NH}_2$, is a colourless, odourless liquid, b. p. 161 – $162^{\circ}/13$ mm.

Triphenylmethylamine hydrochloride is readily decomposed by water at 100° , giving triphenylmethylcarbinol. With $\alpha\alpha$ -diphenylethylamine hydrochloride the decomposition is very slow at 100° , but it proceeds much more rapidly at 200° , a considerable quantity of the unsaturated hydrocarbon being formed. With *tert*-butylamine hydrochloride the decomposition is still more difficult, no change occurring at 160° , but the unsaturated hydrocarbon is formed at 280° after fourteen hours.

With triphenylmethyl chloride in benzene solution, *tert*-butylamine gives triphenylmethyl*tert*-butylamine, $\text{CPh}_3\cdot\text{NH}\cdot\text{CMe}_3$, m. p. 94.5° . A change occurred when this alkyl chloride was heated in benzene solution with phenylisopropylamine, but no product could be isolated.

With silver nitrate the hydrochlorides of these amines give the corresponding nitrites. *tert*-Butylamine nitrite has m. p. 126 – 127° (decomp.), phenylisopropylamine nitrite has m. p. 98 – 99° (decomp.), $\alpha\alpha$ -diphenylethylamine nitrite has m. p. 96 – 97° (decomp.), and triphenylmethylamine nitrite has m. p. 120° (decomp.) when heated quickly.

With benzoyl chloride in dry ethereal solution the four amines gave benzoyl derivatives. *Benzotert*-butylamide, $\text{NHBz}\cdot\text{CMe}_3$, slender needles, has m. p. 136.5° ; benzo- α -phenylisopropylamide, m. p. 159° ; benzo- $\alpha\alpha$ -diphenylethylamide, m. p. 150.5° (decomp.), and benzotriphenylmethylamide, m. p. 165.5° . The amines also react with oxalyl chloride, giving the corresponding oxamides. *N*-*tert*-butyloxamide, $(\text{CMe}_3\cdot\text{NH}\cdot\text{CO})_2$, has m. p. 176° ; di- α -phenylisopropyloxamide, needles, m. p. 131° ; di- $\alpha\alpha$ -diphenylethyloxamide, m. p. 228° ; and ditriphenylmethyloxamide, m. p. 349° . These same oxamides were obtained by the action of ethyl oxalate on the amine, but in this reaction $\alpha\alpha$ -diphenylethylamine gave, in addition, ethyl $\alpha\alpha$ -diphenylethyloxamate, m. p. 134° , which with liquid ammonia yielded $\alpha\alpha$ -diphenylethyloxamide, $\text{CMePh}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$, m. p. 145° , and triphenylmethylamine gave some ethyl triphenylmethyl-oxamate, m. p. 155° (decomp.).

When warmed with potassium cyanate in aqueous solution the

hydrochlorides of the four amines yield the corresponding carbamides, the yield diminishing rapidly in passing up the series from *tert*-butylamine to triphenylmethylamine. *tert*-Butylcarbamide, $\text{CMe}_3\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, has m. p. 183° (Schneegans gives 172° ; compare A., 1894, i, 405); *phenylisopropylcarbamide*, m. p. 191° (decomp.); *aa-diphenylethylcarbamide*, m. p. $206\cdot5^\circ$ (decomp.); *triphenylmethylcarbamide*, m. p. $234\text{--}235^\circ$ (decomp.).

With carbon disulphide in cold ethereal solution, *tert*-butylamine gives a compound, $\text{C}_9\text{H}_{22}\text{N}_2\text{S}_2$, which is probably a combination of the amine with *tert*-butylthiosulphocarbamate. *a*-Phenylisopropylamine reacts less readily, but gives a similar compound, whilst *aa*-diphenylethylamine reacts still more slowly, giving a poor yield of the alkylthiosulphocarbamate. Triphenylmethylamine does not react with carbon disulphide even at 100° . W. G.

Theory of Colour Lakes. I. OSKAR BAUDISCH (*Zeitsch. angew. Chem.*, 1917, 30, I, 133—135).—It is shown that the lakes obtained with various nitrosoarylhydroxylamines can all be explained by Werner's theory, according to which they belong to the group of internal complex salts. The influence of the position of various groups, hydroxyl, nitro, carboxyl, sulphonie (SO_3H), and tolylsulphonyl ($-\text{SO}_2\cdot\text{C}_6\text{H}_5$), in the benzene and naphthalene nuclei is demonstrated by various examples. The pyrazolone and anthraquinone lakes are also shown to conform to Werner's theory.

T. S. P.

The Preparation of the Six Dichlorophenols and some of their Properties. A. F. HOLLEMAN (*Rec. trav. chim.*, 1917, 37, 96—107).—The six dichlorophenols have been prepared, and from them the six dichloroanisoles and the odours of these compounds have been studied. The mixture of 2:4- and 2:6-dichlorophenol obtained in the chlorination of phenol may be readily separated by extraction with a dilute solution of sodium carbonate, the 2:6-dichlorophenol being removed. 2:3-Dichlorophenol, m. p. 57° , can be obtained by diazotising 2:3-dichloroaniline and pouring the product into boiling sulphuric acid (2 acid:1 water). The anisoles were easily obtained from the corresponding phenols by Vermeulen's method (compare A., 1906, i, 256), using methyl sulphate. 2:3-Dichloroanisole has m. p. 31° , 2:4-dichloroanisole, m. p. 28° ; 2:5-dichloroanisole, m. p. 24° ; b. p. $140^\circ/40\text{ mm.}$; 2:6-dichloroanisole, m. p. $10\cdot1^\circ$; 3:4-dichloroanisole, m. p. -8° ; 3:5-dichloroanisole, m. p. 68° . 2:4-Dichlorophenol gives a *benzoyl* derivative, m. p. 96° , and an *amyl ether*, b. p. $172\text{--}173^\circ/15\text{ mm.}$ 2:5-Dichlorophenol gives a *benzoyl* derivative, m. p. 69° .

The odours of these phenols and anisoles have been examined qualitatively, and in the case of the phenols quantitatively, the results being set out in detail in the original. W. G.

Colorimetric Studies of Picrate Solutions. WILLIAM M. DEHN and ALICE A. BALL (*J. Amer. Chem. Soc.*, 1917, 39, 1381—1392).—The colours of solutions of picric acid in 95% alcohol,

water, sodium hydroxide solution, and ammonia solution have been compared with those of solutions in absolute alcohol, and the concentrations of solutions of equal depths of colour are tabulated. It is found that 0.001% solutions in any medium have the same colour, but that in concentrated solutions the intensity of colour is as 1:3.1:10:22.5:24, the order being that of 100% alcohol, 95% alcohol, water, sodium hydroxide, and ammonia solution. The colours of the solutions are enhanced by raising the temperature.

These results are discussed on the basis of the white, benzenoid form of picric acid and the yellow, quinonoid form. White crystals of the acid, even in contact with pyrophosphoric acid, become yellow on treatment with alcohol or water. The change of configuration from benzenoid to quinonoid can, therefore, be brought about by solvents alone, even in the presence of hydrogen ions. Alcohol, water, alkalis, and heat have increasing effects on the rearrangement to the quinonoid type. It may be calculated that about 7860 molecules of water or 20,000 molecules of alcohol are necessary to ensure that every molecule of picric acid is quinonoid. The mechanism of the changes is discussed, and the various theories on the structure of picric acid and picrates are reviewed with extensive references to the literature. J. C. W.

The Crystalline Forms of the Two Naphthols. W. STORTENBEKER (*Zeitsch. Kryst. Min.*, 1916, 55, 373—374).—Groth and Negri state that α -naphthol is monoclinic, but the author confirms Wyrubov's statement that it is rhombic [0.6122:1:0.4236] (compare, however, H. Steinmetz, following abstract). The best crystals were obtained from a mixture of light petroleum and ether.

β -Naphthol crystallises in monoclinic plates [$a:b:c=1.372:1:2.053$; $\beta=60^\circ 10'$]. The ratio $b:c$ appears uncertain, as it is calculated indirectly from a rare form {5 $\bar{2}5$ }, which other observers have not detected. E. H. R.

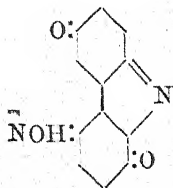
The Crystalline Form of α -Naphthol. H. STEINMETZ (*Zeitsch. Kryst. Min.*, 1916, 55, 375).—A great many solvents were tried in an attempt to get good measurable crystals. The best results were obtained with a mixture of 1 part of acetic acid and 4 to 5 parts of light petroleum, saturated with α -naphthol at 25—30° and cooled slowly to 20°. The crystals obtained were thin plates, quite pure and white. They are monoclinic, prismatic [$a:b:c=2.7483:1:2.7715$; $\beta=117^\circ 10'$]. E. H. R.

Preparation of Halogen Derivatives of Catechol, Homocatechol, and Pyrogallol Methyl Ethers and Sulphonic Acids

ROBERT B. KRAUSS and EDWARD CREDE (*J. Amer. Chem. Soc.*, 1917, 39, 1431—1435).—Brief, practical details are given of the preparation of the following compounds: dibromoguaiacolsulphonic acid (potassium salt, $2H_2O$) and di-iodoguaiacolsulphonic acid (sodium salt, $2H_2O$) from guaiacolsulphonic acid; bromocreosole, $OMe \cdot C_6H_3MeBr \cdot OH$, large rhombs, m. p. 77°, from crude creosote,

b. p. 218—224°; pyrogallol 1:3-dimethyl ether and its sulphonic acid (*barium salt*, $3\text{H}_2\text{O}$); pyrogallol trimethyl ether sulphonic acid (*barium salt*, $2\text{H}_2\text{O}$); dibromopyrogallol sulphonic acid dimethyl ether (*sodium salt*, $2\text{H}_2\text{O}$); *dibromopyrogallol dimethyl ether*, prisms, m. p. 70°; and *dibromopyrogallol trimethyl ether*, m. p. 75—76°.
J. C. W.

3:3'-Diphenol. W. BORSCHÉ (*Ber.*, 1917, **50**, 827—833. Compare Borsche and Scholten, this vol., i, 390).—By conversion into its tetrazo-derivative and subsequent treatment of this with alcohol and copper powder, benzidine-3:3'-disulphonic acid gave diphenyl-3:3'-disulphonic acid, which on fusion with potassium hydroxide at 250° gave 3:3'-diphenol. This substance (Schultz and Kohlhaus, A., 1906, i, 818), on reaction with nitrous acid, did not give the expected diquinonedioxime, but only a poor yield of a brown substance, $\text{C}_{12}\text{H}_6\text{O}_3\text{N}_2$, probably of the annexed constitution. When treated in alkaline solution with an aqueous solution of benzene-diazonium chloride, 3:3'-diphenol was converted into 6:6'-dibenzeneazo-3:3'-diphenol,



$\text{N}_2\text{Ph}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{N}_2\text{Ph}$,
deep yellow leaflets, m. p. 181°; this reacted with methyl sulphate in the presence of aqueous sodium hydroxide, forming its *dimethyl ether*, $\text{C}_{21}\text{H}_{18}\text{O}_2\text{N}_4$, red needles, m. p. 160°, and with alkaline sodium hyposulphite solution, yielding 6:6'-diamino-3:3'-diphenol,

$\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}_2$,
colourless prisms, m. p. 225° (decomp.). In acetic acid solution 3:3'-diphenol reacted with nitric acid, giving 4:6:4':6'-tetranitro-3:3'-diphenol, $\text{OH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{OH}$, yellow needles, m. p. 208.5°, together with a little 2:4:6:4':6'-pentanitro-3:3'-diphenol, $\text{OH}\cdot\text{C}_6\text{H}(\text{NO}_2)_3\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{OH}$, yellow granules, m. p. 248° (decomp.); a much better yield of the tetranitro-compound was obtained on heating 3:3'-dichloro-4:6:4':6'-tetranitrodiphenyl with sodium acetate and acetamide at 200°. The tetranitro- and pentanitro-compounds dissolve in aqueous alkalis and even in hot water, giving yellow solutions, from which they separate again on the addition of mineral acids.

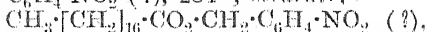
2:4:6:2':4':6'-Hexanitro-3:3'-diphenol,

$\text{OH}\cdot\text{C}_6\text{H}(\text{NO}_2)_3\cdot\text{C}_6\text{H}(\text{NO}_2)_3\cdot\text{OH}$,
yellow, silky needles, m. p. with explosion above 270°, was obtained by the conjoint action of sulphuric acid and nitric acid on 3:3'-diphenol, which also reacted with bromine in acetic acid solution in the presence of a little iron as catalyst with the formation of *hexabromo-3:3'-diphenol*, $\text{C}_{12}\text{H}_4\text{O}_2\text{Br}_6$, colourless needles, m. p. 196°.

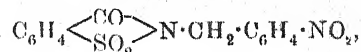
D. F. T.

The State of Saturation of Chromophores. I. LIFSCHITZ (*Ber.*, 1917, **50**, 906—909. Compare Kauffmann, this vol., i, 391).—A reply to Kauffmann's criticisms.
J. C. W.

The Identification of Acids. III. EDWARD LYONS and E. EMMET REID (*J. Amer. Chem. Soc.*, 1917, **39**, 1727—1750. Compare this vol., i, 334).—The application of *p*-nitrobenzyl bromide as a reagent for the identification of acids has been extended to a number of other acids, excellent results being obtained with most of the aromatic acids. Several mixtures of acids have been investigated by this method, and it is found that benzoic acid is readily identified in the presence of acetic, tartaric, citric, salicylic, and *p*-toluenesulphonic acids, and that the sparingly soluble *p*-nitrobenzyl ester of isophthalic acid is readily separable from the acetate, benzoate, and tartrate. The melting points of the esters now described are as follows: *bromoacetate*, 88—89°; *diphenylhydroxyacetate*, 99·5°; *α-amino-n-hexanoate*, 184—185°; *α-amino-β-phenylpropionate*, 221·5°; *α-aminopropionate*, 228—230°; *lactulinate*, 60·5—61°; *hydroxyisobutyrate*, 80·5°; *α-amino-n-butyrate*, 222—223°; *urate*, $C_5H_3O_3N_4 \cdot CH_2 \cdot C_6H_4 \cdot NO_2$ (?), above 305°; *pyromucate*, $C_4H_3O \cdot CO_2 \cdot CH_2 \cdot C_6H_4 \cdot NO_2$ (?), 133·5°; *cyanurate*, $C_3H_2O_3N_3 \cdot CH_2 \cdot C_6H_4 \cdot NO_2$ (?), 284°; *stearate*,

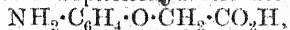


above 285°; *palmitate*, 42·5°; *chlorofumarate*, 138·5°; *dibromosuccinate*, 177·5°; *mucate*, above 310°; *camphorate*, 66·5°; *p-chlorobenzoate*, 129·5°; *m-bromobenzoate*, 104·5°; *m-nitrobenzoate*, 141·5°; *p-nitrobenzoate*, 168·5°; *m-aminobenzoate*, 201°; *2:5-dihydroxybenzoate*, 160°; *2:4-dihydroxybenzoate*, 188—189°; *m-acetylaminobenzoate*, 169·5—170°; *m-acetoxybenzoate*, 140°; *p-toluate*, 104·5°; *p-thioltoluate*, 97°; *o*-, *m*-, and *p*-*ercosates*, 98·5°, 174°, and 147° respectively; *5-iodosalicylate*, 141°; *5-aminosalicylate*, 200·5°; *o*-acetoxybenzoate, 90·5°; *anisate*, 132°; *vanillate*, 140—141°; *piperate*, 145°; *o*-, *m*-, and *p*-*nitrocinnamates*, 132°, 174°, and 186·5° respectively; *coumarate*, 152·5°; *β-hydroxy-naphthoate*, 164°; *o-benzoylsulphinide* derivative,



174·5°; *isophthalate*, 202·5°; *terephthalate*, 263·5°; *4:5-dichlorophthalate*, 164·5°; *tetrachlorophthalate*, 180°; *3-nitrophthalate*, 189·5°; *mellitate*, $C_6(CO_2 \cdot CH_2 \cdot C_6H_4 \cdot NO_2)_6$ (?), 300°. T. H. P.

The Ferrous Sulphate and Ammonia Method for the Reduction of Nitro- to Amino-compounds. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1435—1439).—The authors advocate the wider application of the ferrous sulphate and ammonia method for reducing nitro-compounds, and quote examples of amino-derivatives which are conveniently obtained in this way. These include *m*- and *p*-aminophenylacetic acids; *p*-aminophenoxyacetic acid,



m. p. 220° (evolution of gas, re-solidification; residue not molten at 285°); *o*-aminobenzamide, m. p. 109—111·5°; *m*-aminobenzamide, silky needles, m. p. 113—114° (corr.); *o*-aminobenzoylcarbamide, pale yellow leaflets, comparatively stable in boiling acetic acid (com-

pare Diels and Wagner, A., 1912, i, 512); and *m*-aminobenzoyl-carbamide, which melts at 210° with evolution of gas, resolidifies, and melts again at 275—280°, and is diazotisable. J. C. W.

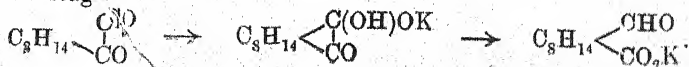
The Action of Alcoholic Ammonia on some Alkylurethanes [Carbamates]. M. BRANDER (*Rec. trav. chim.*, 1917, 37, 88—91).—The carbamates examined were prepared by the action of ethyl chloroformate in ethereal solution on the four primary amines previously described (this vol., i, 555). *Ethyl α-phenylisopropylcarbamate*, $\text{CPhMe}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, crystallises in needles, m. p. 52°; *ethyl αα-diphenylethylcarbamate*, slender needles, has m. p. 66.5°; and *ethyl triphenylmethylcarbamate* has m. p. 112°.

Ethyl tert-butylcarbamate (compare van Erp, A., 1895, i, 587), when heated for twelve hours at 180—185° in a sealed tube with alcoholic ammonia, gives *tert*-butylamine hydrochloride, ethyl carbamate, carbamide, and a trace of *tert*-butylcarbamide. *Ethyl α-phenylisopropylcarbamate* behaves similarly, but gives a larger yield of *α*-phenylisopropylcarbamide. *Ethyl αα-diphenylethylcarbamate* gives none of the corresponding carbamide, whereas *ethyl triphenylmethylcarbamate* gives a considerable amount of *triphenylmethylcarbamide*. W. G.

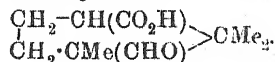
The Action of Sodium Hypochlorite on Amides of Unsaturated Acids. R. A. WEERMAN (*Rec. trav. chim.*, 1917, 37, 1—15).—An extension of previous work (compare A., 1913, i, 1195), four other amides having been studied.

The addition of sodium hypochlorite to a solution of *p*-methoxycinnamamide in methyl alcohol yielded *methyl p-methoxystyrylcarbamate*, colourless needles, m. p. 134—135°, which when moistened with dilute sulphuric acid and distilled in a current of steam gave *p*-methoxyphenylacetaldehyde. *o*-Methoxycoumaramide yielded *methyl trans-o-methoxystyrylcarbamate*, colourless needles, m. p. 114—115°, giving *o-methoxyphenylacetaldehyde*, a colourless oil, b. p. 115—117°/17 mm., yielding an *oxime*, m. p. 94—95°, and a *semicarbazone*, m. p. 158—159°. *o*-Methoxycoumarinamide gave *methyl cis-o-methoxystyrylcarbamate*, m. p. 39—40°, from which *o-methoxyphenylacetaldehyde* can also be prepared. *o-Coumaramide*, rectangular plates, m. p. 208—209°, obtained by the action of ammonia on methyl *o*-coumarate, gave nothing but resinified products under the action of sodium hypochlorite. W. G.

Camphoceanaldehydic Acid (*tert*-sec.) (Camphoric Acid Semialdehyde). J. BREDT (*J. pr. Chem.*, 1917, [ii], 95, 63—74).—When fused with potassium hydroxide and a little water, active or racemic camphorquinone gives a violet-coloured mass, which subsequently becomes colourless; if the heating is discontinued as soon as a small sample of the mixture gives a clear solution in water, the semi-aldehyde of camphoric acid (camphoraldehydic acid) is obtained in good yield, the chemical change probably occurring by the stages



As electrolytic reduction of the product yielded a hydroxyisocampholic acid, the dehydration of which produced β -campholide, the aldehyde and carboxyl groups in the semialdehyde must be situated at the tertiary and secondary carbon atoms respectively, thus:



dl-Camphorquinone, m. p. 199° , prepared by the successive action of sodium-potassium amide and amyl nitrite on *dl*-camphor in the presence of benzene, on fusion with a mixture of equal weights of potassium hydroxide and water at $280\text{--}290^\circ$, yielded *dl*-camphoraldehydic acid, m. p. $61\text{--}64^\circ$; *oxime*, m. p. $148\text{--}149^\circ$; when heated with acetic anhydride at 100° for three to four hours, the aldehyde acid gave *dl*-acetoxy- β -campholide, C_8H_{14} $\begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}(\text{OAc}) \end{array}$ O , m. p. $97\text{--}98^\circ$, b. p. $155\text{--}156^\circ/4\text{ mm.}$, whilst electrolytic reduction in potassium carbonate solution at a potassium amalgam cathode converted it into *dl*- β -campholide, m. p. $216\text{--}217^\circ$.

In a similar manner *d*-camphorquinone was made to yield *d*-camphoraldehydic acid, m. p. $74\text{--}80^\circ$; $[\alpha]_D^{18} + 80.4^\circ$ in methyl alcohol, $+103.0^\circ$ in benzene; *oxime*, m. p. $153\text{--}155^\circ$, b. p. $165^\circ/3\text{ mm.}$, $[\alpha]_D^{18} + 55.67^\circ$ in methyl alcohol; *semicarbazone*, m. p. $195\text{--}196^\circ$ (decomp.). The aldehyde-acid with acetic anhydride yielded *l*-acetoxy- β -campholide, m. p. $124\text{--}125^\circ$, $[\alpha]_D^{18} - 78.3^\circ$ in benzene, and on reduction gave *d*- β -campholide, m. p. $216\text{--}217^\circ$, $[\alpha]_D^{18} + 35.6^\circ$ in methyl alcohol, $+46.08^\circ$ in benzene (compare Haller and Blanc, A., 1905, i, 858).

The indefinite m. p.'s of the active and racemic forms of camphoraldehydic acid are probably to be attributed to the presence of *cis-trans*-isomerides.

dl- α -Campholide, m. p. $210\text{--}211^\circ$, was obtained by oxidation of *dl*-camphor with potassium persulphate. The active and inactive modifications of α -campholide are readily distinguished from the β -campholides by the fact that they react with an acetic acid solution of hydrogen bromide, yielding bromocampholic acid, whereas the β -isomerides are unaffected. D. F. T.

The Crystalline Form of Phenylglyceric Acid and its Active Components. V. M. GOLDSCHMIDT (*Zeitsch. Kryst. Min.*, 1915, 55, 123--131).—Inactive phenylglyceric acid melts at 141° , whilst its *lævo*- and *dextro*-components melt at $164\text{--}165^\circ$. An examination of the crystals of the active and inactive forms of the acid has been made with the object of determining whether the latter is a true or pseudo-racemic compound.

The crystals of the *d*- and *l*-active forms belong to the monoclinic-sphenoidal class, and are enantiomorphous, but otherwise identical. The axial ratios are $[a:b:c=2.1875:1.20794; \beta=93^\circ 53']$, $D\ 1.451$, and the crystals have a good cleavage parallel to $\{100\}$ and less perfect cleavages parallel to $\{001\}$ and $\{110\}$. Their enantiomorphous character is clearly shown by etching with methyl alcohol.

The crystals of the inactive form are similar in habit to those of

the active form, have the same density and axial ratios, but appear to belong to the prismatic class of the monoclinic system, since the faces which reveal the enantiomorphous character of the active crystals are lacking. The etched figures, however, are of the same enantiomorphous character as those of the active crystals, and indicate clearly that the inactive crystals are made up of parallel layers on the face {100} of equal quantities of the right- and left-handed crystals. This conclusion was confirmed by crystallising the inactive acid from various solvents, when sometimes active right- and left-handed crystals were obtained.

The lower melting point of the inactive acid is in agreement with Roozeboom's generalisation, that the melting-point curve of a system of optical antipodes which form neither true mixed crystals nor a true racemic compound must show a temperature minimum with equal quantities of the two antipodes. The author has examined the melting-point curve of mixtures of *D*- and *L*-phenylglyceric acids, and finds a minimum at 141° with 50% of each component.

It is suggested that pseudo-racemic crystals should be divided into two classes:

A. Pseudo-racemic mixed crystals, that is, isomorphous mixtures of equal quantities of *D*- and *L*-substance, the melting-point curve varying continuously, as in camphoroxime.

B. Pseudo-racemic conglomerates, lamellar growths of equal quantities of both antipodes, an example of which we have in phenylglyceric acid.

E. H. R.

Resolution of the Phenylglyceric Acid with m. p. 122° into its Optically-active Components. C. N. RIEBER and E. BERNER (*Ber.*, 1917, **50**, 893—897).—Two years ago the resolution of phenylglyceric acid of m. p. 141° was described (*A.*, 1915, i, 544), and it was then assumed that the acid with m. p. 122° had already been resolved by Plöchl and Mayer (*A.*, 1897, i, 528). It has now been found that these authors were in error. They reported that their active acids of m. p. 167° did not unite to form the racemate, but the new acids of m. p. 95° are found to do so in the normal way. Transformation into the active components of the acid with m. p. 141° must have taken place.

Phenylglyceric acid, m. p. 122°, is resolved by taking advantage of the fact that the strychnine salt of the *D*-acid is the less soluble in alcohol. The *D*-acid has m. p. 95°, $[\alpha]_D^{20} + 26.11^\circ$, $[\alpha]_D^{20} + 20.19^\circ$, $[\alpha]_F^{20} + 34.48^\circ$ in water, $[\alpha]_D^{20} + 21.15^\circ$ in 97% alcohol, $[\alpha]_D^{20} + 27.49^\circ$ in acetone, and crystallises in needles, tablets, or prisms of the monoclinic-sphenoidal class $[a:b:c = 2.5408:1:2.2216; \beta = 90^\circ 40']$. The *L*-acid has m. p. 97—98°, $[\alpha]_D^{20} - 25.6^\circ$.

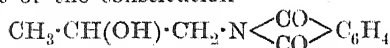
The racemic acid, m. p. 122°, exists in two enantiomorphous forms $[a:b:c = 2.5605:1:1.7251; \beta = 101^\circ 27']$.

The following table gives the number of grams of the acids which dissolve in 100 grams of dry ether at 20°:

	Inactive.	<i>D</i> -Acid.	<i>L</i> -Acid.
Phenylglyceric acid, m. p. 122° ...	2.78	9.02	—
Phenylglyceric acid, m. p. 141° ...	1.08	0.80	0.48

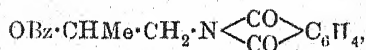
J. C. W.

n- and *iso*Propylamine. S. GABRIEL and HEINZ OHLE (*Ber.*, 1917, **50**, 804—818).—An endeavour to convert β -chloro-*n*-propyl alcohol into the corresponding hydroxyisopropylamine by the potassium phthalimide method unexpectedly gave rise to the *n*-propylamine compound. This is found to be due to the primary elimination of hydrogen chloride from the halogen compound under the influence of the potassium phthalimide with the formation of propylene oxide, which then reacts additively with the phthalimide, giving a product of the constitution



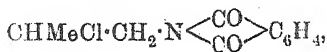
(see following abstract). A similar observation that β -chloro-*n*-propyl acetate likewise yielded the phthalimide derivative corresponding with β -acetoxy-*n*-propylamine is attributed to the presence of some chloroisopropyl acetate in the original β -chloro-*n*-propyl acetate, again probably due to the partial intermediate formation of propylene oxide during the treatment of chloroisopropyl alcohol with potassium acetate, the unaltered compound yielding acetoxyisopropyl alcohol, whereas the propylene oxide combines with acetic acid, giving rise to β -acetoxy-*n*-propyl alcohol; when this mixture is submitted to the action of hydrogen chloride, a mixture of two chloro-isomerides is obtained, which have almost the same b. p. and are not easily separable by distillation. In an attempt to obtain the desired chlorohydroxypropane derivatives in a pure condition, chloroisopropyl alcohol was made to react with potassium benzoate and the hydroxyl group of the product was then displaced by bromine in the hope of obtaining solid substances purifiable by crystallisation; the products, however, were liquids, and investigation showed that in these the benzyloxy-group was present to a considerable extent at the β -position, this result again indicating the intermediate occurrence of propylene oxide.

β -Hydroxy-*n*-propylphthalimide has m. p. 88—90° (Mendelssohn-Bartholdy, *A.*, 1907, i, 1043, gives m. p. 73°), whether prepared from β -chloroisopropyl alcohol or β -chloro-*n*-propyl alcohol. β -Acetoxy-*n*-propylphthalimide, $\text{OAc} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{N} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C}_6\text{H}_4$, needles, m. p. 99—100°, obtained by the interaction of potassium phthalimide and Henry's " β -chloro-*n*-propyl acetate" (*A.*, 1903, i, 725), on hydrolysis gave α -aminoisopropyl alcohol (*hydrochloride*, m. p. 72.5—74°; *sodium picrate*, $\text{OH} \cdot \text{C}_3\text{H}_6 \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_5 \cdot \text{O}_7\text{N}_3 \cdot \text{C}_6\text{H}_5 \cdot \text{O}_7\text{N}_3 \cdot \text{Na}$, m. p. 177—178°). β -Benzyloxy-*n*-propylphthalimide,

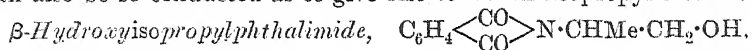


leaflets, m. p. 115—116°, obtained by the successive action of potassium benzoate, hydrobromic acid, and potassium phthalimide on β -chloroisopropyl alcohol, can also be formed from β -hydroxy-*n*-propylphthalimide by treating with hydrobromic acid and potassium benzoate successively. Hydrolysis of β -benzyloxy-*n*-propylphthalimide with hydrochloric acid in solution in acetic acid yields β -chloro-*n*-propylamine, $\text{CHMeCl} \cdot \text{CH}_2 \cdot \text{NH}_2$ (*hydrochloride*, crystalline powder, m. p. 183.5—186°; *picrate*, rhombic tablets and cubes,

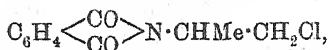
m. p. 154·5—155·5°; *platinichloride*, needles, m. p. 221—225°, decomp.); the hydrochloride of this base, when heated with phthalic anhydride, is converted into β -chloro-*n*-propylphthalimide,



needles, m. p. 100—102°, identical with the product of interaction between β -hydroxy-*n*-propylphthalimide (above) and phosphorus pentachloride. The hydrolysis of β -benzoyloxy-*n*-propylphthalimide can also be so conducted as to give rise to α -aminoisopropyl alcohol.

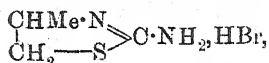


long, hexagonal leaflets, m. p. 99—101°, obtained by the action of phthalic anhydride on an alcoholic solution of β -amino-*n*-propyl alcohol (hydroxyisopropylamine), reacts with phosphorus pentachloride, giving β -chloroisopropylphthalimide,

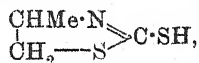


leaflets, m. p. 56—58°, and with phosphorus pentabromide yielding the corresponding β -bromo-derivative, tablets, m. p. 59—60°.

β -Bromoisopropylamine hydrobromide when treated in hot aqueous solution with potassium thiocyanate, undergoes conversion into 2-amino-4-methylthiazoline hydrobromide,



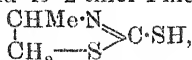
needles, m. p. 128—129° (*picrate*, yellow, crystalline powder, m. p. 230—244°, decomp.), whilst on treatment with a solution of sodium hydroxide (2 molecules) and with carbon disulphide (1 molecule) successively, it gives rise to 2-thiol-4-methylthiazoline



rhombic needles and leaflets, m. p. 98·5—99°.

Contrary to the belief of Gabriel and von Hirsch (A., 1897, i, 135), β -bromopropylamine and β -bromoisopropylamine, when made to eliminate hydrogen bromide and then to recombine with this compound, both yield β -bromoisopropylamine, this result being explicable by the intermediate compound being propyleneimine, $\begin{array}{c} \text{CHMe} \\ | \\ \text{CH}_2 \end{array} \begin{array}{c} \diagup \text{N} \\ \diagdown \end{array} \text{NH}$, and not *isoallylamine*, $\text{CHMe} : \text{CH} \cdot \text{NH}_2$. In a similar manner, the products of the action of hydrogen chloride and hydrogen iodide on the propyleneimine are to be regarded as β -chloroisopropylamine and β -iodoisopropylamine, the *picrate* of the former having m. p. 145—146° (Gabriel and von Hirsch, *loc. cit.*, give m. p. 158°). The identity of the intermediate compound as propyleneimine, and not *isoallylamine*, is further confirmed by a demonstration that the additive compound with sodium hydrogen sulphite is not β -methyltaurine, m. p. 290—293° (Gabriel and Colman, A., 1906, i, 889), but has m. p. 323° (decomp.), and is

actually *isopropylamine-β-sulphonic acid*, whilst the carbon disulphide additive compound is 2-thiol-4-methylthiazoline,

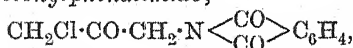


and not the 2-thiol-5-methyl isomeride.

D. F. T.

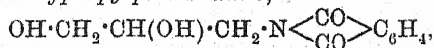
Preparation of Primary Alkylamines. S. GABRIEL and HEINZ OHLE (*Ber.*, 1917, 50, 819—825. Compare preceding abstract).—Whereas ethylene oxide and its homologues react with ammonia, yielding a mixture of primary, secondary, and tertiary alkylamines, it is possible to effect the combination of these oxides with phthalimide, with the formation of products from which a pure primary alkylamine can be obtained by hydrolysis.

Ethylene oxide and propylene oxide in this way give rise to *β-hydroxyethylphthalimide* and *β-hydroxypropylphthalimide* respectively. Epichlorohydrin yields *γ-chloro-β-hydroxypropylphthalimide*, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{N} \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$, a colourless, crystalline powder, m. p. 95—96·5°, the constitution of which is indicated by its further conversion into *βγ-dichloropropylphthalimide* on treatment with phosphorus pentachloride, and into *β-hydroxytrimethylenediphthalimide* by further treatment with potassium phthalimide. *γ-Chloro-β-hydroxypropylphthalimide* reacts with alcoholic sodium iodide, giving rise to *γ-iodo-β-hydroxypropylphthalimide*, $\text{CH}_2\text{I}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{N} \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$, needles, m. p. 123—124°; when warmed with potassium hydroxide solution and then treated with sodium nitrite and hydrochloric acid, it is converted into the *nitrosoamine* of *βγ-dihydroxypropylphthalamic anhydride*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO}-\text{O}-\text{CH}_2 \\ \diagup \diagdown \\ \text{CO}\cdot\text{N}(\text{NO})\cdot\text{CH}_2 \end{smallmatrix} \text{CH}\cdot\text{OH}$, prisms, m. p. 104° (compare Gabriel, A., 1905, i, 650); chromic acid effects its oxidation to *γ-chloroacetylphthalimide*,

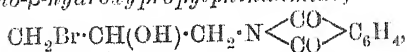


needles, m. p. 139·5°, whilst hydrochloric acid causes its hydrolysis to *β-chloro-β'-aminoisopropyl alcohol*; *hydrochloride*, leaflets, m. p. 103—104°; *picrate*, m. p. 159·5—160·5°; *platinichloride*, needles, m. p. 214—216° (decomp.); the *benzoyl* derivative, leaflets, m. p. 103°, on boiling with water is converted into oily *γ-amino-β-hydroxypropyl benzoate*, $\text{OBz}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NH}_2$ (*hydrochloride*, crystals, m. p. 164·5°; *aurichloride* and *platinichloride*, crystalline), whilst when boiled with aqueous potassium hydroxide it yields *5-hydroxy-2-phenylpentoxazoline*, $\text{CPh} \begin{smallmatrix} \text{N}\cdot\text{CH}_2 \\ \diagup \diagdown \\ \text{O}\cdot\text{CH}_2 \end{smallmatrix} \text{CH}\cdot\text{OH}$, needles, m. p. 98°.

The interaction of glycidic and phthalimide at 120—130° produces *βγ-dihydroxypropylphthalimide*,



leaflets, m. p. 111.5—112.5°, which reacts with hydrobromic acid at 170°, giving β -dibromopropylamine hydrobromide, and at 100° forming γ -bromo- β -hydroxypropylphthalimide,



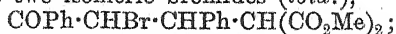
m. p. 114—114.5°; this on treatment with potassium phthalimide yields β -hydroxytrimethylenediphthalimide. D. F. T.

The cycloPropane Series. E. P. KOHLER and J. B. CONANT (*J. Amer. Chem. Soc.*, 1917, **39**, 1404—1420).—An account of the

reactions of compounds of the type $(\text{CO}_2\text{R})_2\text{C}\begin{matrix} 1 & 2 \\ & \diagup \quad \diagdown \\ & \text{CHPh} \\ & \text{CHBz} \\ & 3 \end{matrix}$ In some

respects, notably in their stability towards permanganate, ozone, or bromine, these compounds behave quite differently from ethylenes, but in others they resemble $\alpha\beta$ -unsaturated ketones and acids, particularly in being attacked very readily by halogen hydrides, nascent hydrogen, bases, and metallic derivatives. With these agents, it is possible to effect a rupture of the ring at each of the three points. Nascent hydrogen opens the ring between atoms 1 and 3, alkyl oxides, ammonia, and amines rupture the ring between 1 and 2, and halogen hydrides dissolved in glacial acetic acid attack the 2:3-position. These reactions show that a cyclopropane ring and a ketonic group in the above juxtaposition behave like a conjugate system.

The particular substance from which the present cyclopropane derivatives were obtained was methyl γ -benzoyl- β -phenylethylmalonate (A., 1911, i, 984). This is best prepared by adding sodium methoxide solution to a mixture of phenyl styryl ketone and methyl malonate until the reaction is just distinctly alkaline. The ester forms two isomeric bromides (*ibid.*),

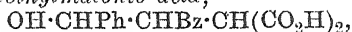


the one with m. p. 113° is best formed by brominating in chloroform at -10°, the other, m. p. 98°, by exposing a suspension of the ester in dry methyl alcohol and bromine to sunlight. Many substances remove the elements of hydrogen bromide from these compounds, with the formation of stereoisomeric cyclopropane derivatives, but a slight excess of magnesium methoxide gives the purest products. Methyl 3-benzoyl-2-phenylcyclopropanedicarboxylate crystallises in large tablets, m. p. 72° (from the bromide with m. p. 98°), or plates, m. p. 92° (from the less fusible bromide). The compound previously considered to be methyl γ -benzoyl- β -phenylvinylmalonate was really the cyclopropane derivative, m. p. 92°.

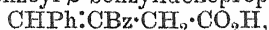
The two esters are hydrolysed to the same methyl hydrogen ester (needles from diluted methyl alcohol, large prisms from chloroform, m. p. 155°) by leaving an ethereal solution in contact with a slight excess of sodium methoxide for a few minutes. This ester yields the di-ester, m. p. 72°, when re-esterified, and may be further hydrolysed by alcoholic potassium hydroxide to γ -benzoyl-

β -phenylcyclopropanedicarboxylic acid, which is best obtained in the two stages, and was originally supposed to be γ -benzoyl- β -phenylbutyrolactonic acid.

The dimethyl esters suffer rupture of the ring when treated with anhydrous alkaline agents, but partial hydrolysis usually happens as well. Magnesium methoxide gives the best results. When a solution of either ester in dry methyl alcohol is boiled with this agent as long as the yellow magnesium compound which is formed seems to increase, it yields methyl β -benzoyl- γ -phenylvinylmalonate, $\text{CHPh}\cdot\text{CBz}\cdot\text{CH}(\text{CO}_2\text{Me})_2$, in plates, m. p. 119° , whilst a geometric isomeride, m. p. 147° , is produced if the action is prolonged to some hours. These esters yield the same γ -hydroxy- β -benzoyl- γ -phenylethylmalonic acid,

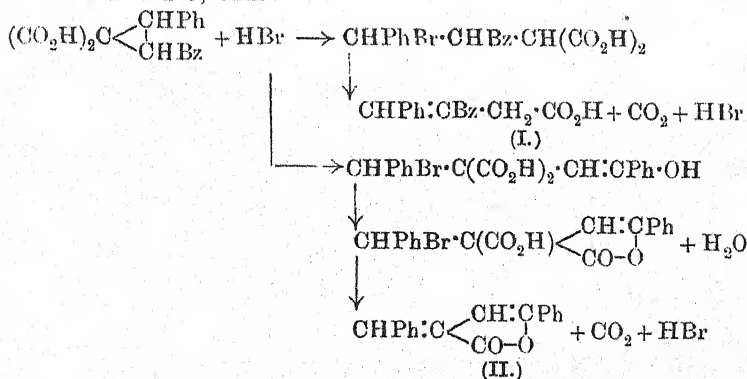


on addition to 20% sodium hydroxide and boiling for a few minutes. The acid crystallises in long, slender needles, m. p. 125° (decomp.), yields the ester with m. p. 147° when esterified, is decomposed into benzaldehyde and β -benzoylpropionic acid if boiled too long with water or bases, and gives β -benzoyl- γ -phenylisocrotonic acid (β -benzoyl- β -benzylidenepropionic acid),



m. p. 131° (compare Borsche, A., 1914, i, 686), on heating at 100° for a few hours. The two esters also behave alike towards permanganate. In moist acetone they yield benzoic acid and carbon dioxide, but in dry acetone they take up one atomic proportion of oxygen only, and form a sparingly soluble substance, m. p. 220° (decomp.).

γ -Benzoyl- β -phenylcyclopropanedicarboxylic acid reacts with a solution of hydrogen bromide in glacial acetic acid when left in the cold for some weeks to form the above β -benzoyl- γ -phenylisocrotonic acid (I) and yellow α -benzylidene- γ -phenylcrotonolactone (II), m. p. 150° (*ibid.*), which are separated by fractional crystallisation. These are obviously secondary products, but the production of the first can be traced to a rupture of the ring between carbon atoms 1 and 2, and that of the second to an attack between 2 and 3, thus:



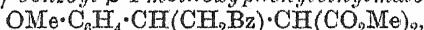
The action of heat on γ -benzoyl- β -phenylcyclopropanedicarboxylic acid was investigated earlier, but the results were misinterpreted. Six products have been separated and identified, namely: (1) the above benzoylphenylisocrotonic acid, previously called benzoylphenylvinylacetic acid; (2) an α -phenacylcinnamic acid, m. p. 180° ; (3) 3-benzoyl-2-phenylcyclopropane-1-carboxylic acid, long, silky needles, m. p. 150° ; (4) and (5) isomeric α -benzylidene- γ -phenylcrotonolactones, m. p. 150° and 180° , both yellow; and (6) β -benzoyl- γ -phenylbutyrolactone, m. p. 93° . Three distinct reactions are involved in the production of these compounds.

The various cyclopropane derivatives are readily reduced by means of zinc dust and acetic acid to the esters of γ -benzoyl- β -phenylethylmalonic acid, or the acid itself, as the case may be.

J. C. W.

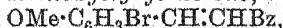
The cycloPropane Series. II. E. P. KOHLER and J. B. CONANT (J. Amer. Chem. Soc., 1917, 39, 1699—1715).—Further investigations (compare preceding abstract) have been made with methyl 3-benzoyl-2-*m*-bromo-*p*-methoxyphenylethylmalonate-1:1-dicarboxylate and its derivatives. The results show that the ring in these compounds is more or less easily opened by reducing agents, halogen hydracids, bases, the Grignard reagent, or phosphorus pentachloride, and that it is possible to open the ring in three different ways. The primary reaction between the cyclopropane derivative and any reagent is similar to that between the corresponding ethylenic compound and the same reagent. These cyclopropane derivatives exhibit, indeed, all the peculiarities of ethylenic compounds containing conjugated systems of double linkings, but they do not, like many ethylenic compounds, combine with the halogens or reduce permanganate.

Addition of methyl malonate to phenyl *p*-methoxystyryl ketone yields methyl γ -benzoyl- β -4-methoxyphenylethylmalonate,

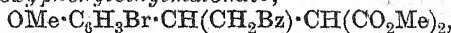


m. p. 80° , or (+1Et·OH), 66° , or (+1Me·OH), 58° , but the cyclopropane compound could not be obtained from this compound.

Phenyl *m*-bromo-*p*-methoxystyryl ketone,



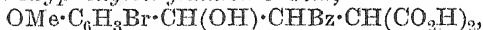
prepared from bromoanisaldehyde and acetophenone in the presence of sodium hydroxide, forms yellow needles, m. p. 107° , and unites with two atoms of bromine, giving phenyl $\alpha\beta$ -dibromo- β -*m*-bromo-*p*-methoxyphenylethyl ketone, m. p. 179° . Addition of the unsaturated ketone to methyl malonate yields methyl γ -benzoyl- β -3-bromo-4-methoxyphenylethylmalonate,



which forms slender, white needles, m. p. 125° ; the corresponding potassium salt decomposes at 185° . The action of bromine on the malonic derivative yields an oily bromo-compound, which, when boiled with potassium acetate in methyl-alcoholic solution, is converted into methyl 3-benzoyl-2-*m*-bromo-*p*-methoxyphenylethylmalonate-1:1-dicarboxylate, $\text{CHBz} < \begin{array}{c} \text{CH} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{OMe} \\ \text{C}(\text{CO}_2\text{Me})_2 \end{array}$, which forms

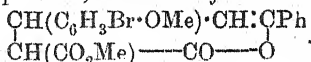
long needles, m. p. 153°. Reduction of this ester by means of zinc dust and acetic acid gives the original saturated ketonic ester. The corresponding *methyl hydrogen ester*, $C_{20}H_{17}O_6Br$, forms needles, m. p. 178° (decomp.), and the acid, $C_{18}H_{15}O_6Br$, has m. p. 210—220° (decomp.).

The action of calcium or magnesium methoxide on the methyl ester yields: (1) an *isomeric cyclopropane ester*, needles, m. p. 129°, and (2) *methyl β-benzoyl-γ-3-bromo-4-methoxyphenylvinylmalonate*, $OMe \cdot C_6H_3Br \cdot CH : CBz \cdot CH(CO_2Me)_2$, cubical crystals, m. p. 129°, and an *isomeric unsaturated ester*, needles, m. p. 139°. In acetone containing a little water or acetic acid, these two unsaturated esters are rapidly oxidised by permanganate to benzoic and bromoanisic acids, whereas in absence of water the product is a crystalline substance, m. p. 245° (decomp.), which was not further investigated. Hydrolysis of the esters gives *γ-hydroxy-β-benzoyl-γ-3-bromo-4-methoxyphenylethylmalonic acid*,

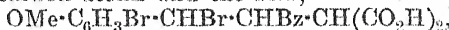


m. p. 144°. When boiled with water, the latter loses water and carbon dioxide, giving *β-benzoyl-γ-3-bromo-4-methoxyphenylvinylacetic acid*, $OMe \cdot C_6H_3Br \cdot CH : CBz \cdot CH_2 \cdot CO_2H$, m. p. 178—180°, which rapidly reduces permanganate, but does not combine with bromine, and may also be obtained synthetically from methyl β-benzoylpropionate and bromoanisaldehyde.

When phenyl α-bromo-β-phenylethyl ketone is treated with ethyl sodiomalonate and the resulting unsaturated ketone reduced with hydrogen in the presence of colloidal palladium, the saturated ketone so produced treated with bromine, and the product condensed with methyl sodiomalonate, an oil is obtained which, when shaken with sodium methoxide and the product acidified, gives a colourless solid, m. p. 116°, which may be the *lactone*,



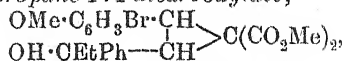
The above *cyclopropane esters or acids* are attacked by hydrobromic acid in glacial acetic acid, the ring being opened between the 1- and 2-carbon atoms and the *acid*,



formed. When heated with a dilute acid, the calcium salt of this acid gives an oily lactone, which is converted by methyl-alcoholic potassium hydroxide into the monobasic unsaturated acid, m. p. 178° (see above), and a minute quantity of the acid, m. p. 155—156°.

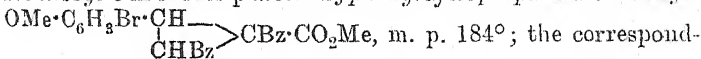
The action of phosphorus pentachloride on the *cyclopropane acid* yields the *lactone*, $OMe \cdot C_6H_3Br \cdot CH : C \begin{array}{l} \text{CH:C} \\ \text{CO-O} \end{array}$, canary-yellow needles, m. p. 197°, which may also be prepared by heating a mixture of sodium γ-phenylisocrotonate, bromoanisaldehyde, and acetic anhydride. Treatment with sodium methoxide converts the lactone into *β-benzyl-α-3-bromo-4-methoxybenzylidenepropionic acid*, $OMe \cdot C_6H_3Br \cdot CH : C(CH_2Bz) \cdot CO_2H$, m. p. about 155°, which is rapidly re-converted into the lactone by acids.

The action of magnesium ethyl bromide on the *cyclopropane* ester yields: (1) *methyl 2-m-bromo-p-methoxyphenyl-3-α-hydroxy-α-phenylpropylcyclopropane-1:1-dicarboxylate*,



m. p. 135°, and (2) a small proportion of an isomeric ester, m. p. 161°.

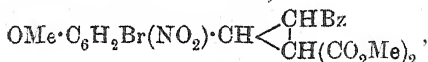
Similarly, the action of magnesium phenyl bromide yields *methyl 1:2-dibenzoyl-3-m-bromo-p-methoxyphenylethylcyclopropane-1-carboxylate*,



ing acid, $\text{C}_{25}\text{H}_{19}\text{O}_5\text{Br}$, m. p. 175°, remains undecomposed at 220°. Reduction of the ester, m. p. 184°; by means of zinc dust and acetic acid yields *methyl α-γ-dibenzoyl-β-3-bromo-4-methoxyphenylbutyrate*, $\text{CO}_2\text{Me} \cdot \text{CHBz} \cdot \text{CH}(\text{CH}_2\text{Bz}) \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{OMe}$, m. p. 182°, the corresponding acid having m. p. 135° (decomp.).

Methyl β-benzoyl-γ-phenyl-γ-3-bromo-4-methoxyphenylethylmalonate, $\text{OMe} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CHPh} \cdot \text{CHBz} \cdot \text{CH}(\text{CO}_2\text{Me})_2$, m. p. 176°, is obtained in small yield when the *cyclopropane* ester is treated with an excess of ice-cold magnesium phenyl bromide; oxidation of the corresponding acid with chromic acid gave no definite products. [3-Bromo-4-methoxybenzophenone, prepared by brominating 4-methoxybenzophenone, has m. p. 69°.]

The action of nitric acid on the *cyclopropane* ester, m. p. 153°, yields: (1) the *nitro*-substituted ester,



m. p. 113°; the corresponding *methyl hydrogen* ester, $\text{C}_{20}\text{H}_{16}\text{O}_8\text{NBr}$, was also prepared; (2) a small quantity of a yellow compound, m. p. 223°. T. H. P.

The Pungent Principles of Ginger. I. A New Ketone, Zingerone[4-Hydroxy-3-methoxyphenylethyl Methyl Ketone] Occurring in Ginger. HIROSHI NOMURA (T., 1917, 111, 769—776).—By extracting dry ginger with ether in the cold, a syrup was obtained which was extracted with sodium hydroxide and precipitated by carbon dioxide. An oil was ultimately obtained amounting to about 1 per cent. of the original ginger. From this a ketone, m. p. 40—41°, was extracted by sodium hydrogen sulphite. This ketone, *zingerone*, forms a *benzoyl* derivative, m. p. 126—127°, an *acetyl* derivative, b. p. 204—205°/14 mm., m. p. 40—42°, and a *methyl* derivative, b. p. 186°/16 mm., m. p. 55—56°, of which the *oxime* melts at 93—93.5°. Ethylation yields *ethylzingerone*, m. p. 66°. Methylzingerone oxidised with potassium permanganate yielded veratric acid, whilst with sodium hypochlorite, veratric acid and another acid, m. p. 95—99°, probably β-3:4-dimethoxyphenylpropionic acid, were obtained. With sodium hypobromite, bromoform and β-3:4-dimethoxyphenylpropionic acid were formed. Oxidation of ethyl

zingerone with sodium hypochlorite yielded ethylvanillic acid. These experiments indicate that zingerone is 4-hydroxy-3-methoxyphenylethyl methyl ketone, and this was corroborated by synthesis. Vanillin and acetone on condensation yield 4-hydroxy-3-methoxystyryl methyl ketone, which by reduction with hydrogen in the presence of platinum-black yielded synthetic zingerone.

T. S. PA.

The Pungent Principle of Ginger. I. The Chemical Characters and Decomposition Products of Thresh's "Gingerol," ARTHUR LAPWORTH, (MRS.) LEONORE KLETZ PEARSON, and FRANK ALBERT ROYLE (T., 1917, 111, 777—790).—In continuation of the work of Garnett and Grier, the authors have examined the oleo-resin gingerol first investigated by Thresh. The residue from an alcoholic extract of ginger was purified by re-extraction with alcohol and with hot petroleum. The purest material thus obtained was a viscous, faintly yellow oil entirely soluble in dilute aqueous alkali. It distilled in the cathode ray vacuum from a bath at a temperature of 135—140°. The pure samples do not give a crystalline product with sodium hydrogen sulphite, but do so after distillation and other treatment. Gingerol has a phenolic character and can easily be methylated with methyl sulphate. The methylgingerol obtained melted at 64° and is optically active, $[\alpha]_D^{20}$ (chloroform, $p=2$), +27.3°. Methylgingerol forms an oxime hydrate and appears also to contain another hydroxyl group. Oxidation of gingerol with chromic acid yielded mainly *n*-heptoic, and probably *n*-hexoic, acid, whilst methylgingerol on oxidation yielded the same mixture of fatty acids along with veratric acid. Samples of gingerol which had been distilled under diminished pressure yield, on steam distillation, some heptaldehyde, whilst from the residue sodium hydrogen sulphite extracts a ketone which can be liberated as a sweet-smelling oil with a very pungent taste. This ketone, zingerone, is most readily obtained by decomposing gingerol with hot baryta water into aldehydes, mainly volatile in steam, and the new ketone. Methylgingerol decomposes in much the same way to give methylzingerone. Zingerone is a colourless solid, m. p. 31—34°, only slightly volatile in steam. It has a phenolic character and forms a *phenylhydrazone*, m. p. about 143°, a *semicarbazone*, m. p. about 133°, and an *ethylcarbonato*-derivative, m. p. 45—47°. Methylzingerone was also prepared by methylation of zingerone with methyl sulphate, m. p. 55.5—56.2°. The methyl derivative has no phenolic properties; when oxidised with permanganate it gives veratric acid, m. p. 179°; it forms an oxime, m. p. 91—92°. Methylzingerone warmed with aqueous sodium hypobromite yielded bromoform and β -3:4-dimethoxyphenylpropionic acid, whence zingerone is probably 4-hydroxy-3-methoxyphenylethyl methyl ketone. It appears, therefore, that the oleo-resin gingerol is essentially a mixture of optically active saturated phenolic compounds derived from a residue of zingerone associated with a

molecular proportion of the residue of a saturated aliphatic aldehyde which in the main constituent is *n*-hexaldehyde.

T. S. PA.

The Pungent Principle of Ginger. II. Synthetic Preparations of Zingerone, Methylzingerone, and some Related Acids. ARTHUR LAPWORTH and FREDERICK HENRY WYKES (T., 1917, 111, 790—798).—Methylzingerone was readily synthesised by reduction of the 3:4-dimethoxystyryl methyl ketone formed by the interaction of veratraldehyde and acetone. The corresponding synthesis of zingerone from vanillin offered difficulties, but it was found that vanillin could be readily converted into ethyl vanillylideneacetate, which was reduced by means of sodium amalgam, the product with excess of alkali yielding an acid, doubtless vanillylacetoacetic acid, which when heated lost carbon dioxide and was converted into zingerone. The authors' work included syntheses of hydroferulic acid and hydrocaffeic acid. In the former case, vanillin was converted into ethyl vanillylidene-malonate or ethyl vanillylidene-cyanoacetate, which was then reduced at the double bond, and on hydrolysis yielded an acid, vanillylmalonic acid, which on heating gave hydroferulic acid. A similar process with protocatechualdehyde gave hydrocaffeic acid. Hydroferulic acid is easily converted into hydrocaffeic acid by heating it with dilute hydrochloric acid at 200°. T. S. PA.

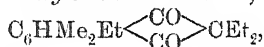
Gingerol and Paradol. E. K. NELSON (*J. Amer. Chem. Soc.*, 1917, 39, 1466—1469).—Some notes on the pungent principles of ginger and grains of paradise (*Amomum melegueta*). In view of Lapworth's researches (T., 1917, 111, 777—798), the work has been discontinued. Gingerol and paradol yield the same dimethyl ether, but the latter is the more stable towards boiling 2*N*-alcoholic potassium hydroxide. They appear to be isomeric monomethyl ethers of the same dihydric phenol. J. C. W.

Preparation of α -Benzildioxime. K. VON AUWERS (*Ber.*, 1917, 50, 952—953. Compare Grossmann and Mannheim, this vol., ii, 391).—The author points out that the process suggested by Grossmann and Mannheim for the preparation of α -benzildioxime was already described by him in 1888, and that Atack's method (A., 1913, ii, 730) is not so unsuitable as these authors suppose. J. C. W.

Synthesis of Indandiones. VI. MARTIN FREUND and KARL FLEISCHER [Sections I.—IV. with EDUARD GOFFERJÉ, V. with JOHANN STEMMER] (*Annalen*, 1917, 414, 1—53. Compare A., 1916, i, 317, and earlier, and for nomenclature Ephraim, A., 1901, i, 688).—The synthesis of indandiones has now been extended to systems in which there is not only one five-membered ring condensed with a benzene nucleus, but two, in the two possible ways, and even three. The authors propose a new nomenclature for the series, referring to the parent hydrocarbons as benzhydrindene,

symmetrical and vicinal benzdihydrindenes, and benztrihydrindene.

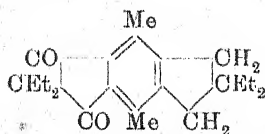
I. *A New Method for the Preparation of Benzenepentacarboxylic Acid*.—The oxidation of an alkylated indandione, if a suitable one can be found, offers a convenient method for the preparation of a benzene polycarboxylic acid, and such a synthesis is readily carried through in the case of benzenepentacarboxylic acid. *p*-Xylene is condensed with acetyl chloride to form 2:5-dimethylacetophenone, b. p. 224—225°; this is reduced by Clemmensen's method to 1:4-dimethyl-2-ethylbenzene, b. p. 185—186°, D^{20}_D 0.8750, n_D 1.5051, and this is condensed with diethylmalonyl chloride under the influence of aluminium chloride. The product, 4:7-dimethyl-2:2:5-triethylindan-1:3-dione,



is a pale yellow, viscous, aromatic oil, b. p. 183—184°/11 mm., D 1.033, which yields benzenepentacarboxylic acid, m. p. 238°, when heated with fuming nitric acid at 140° for seven hours. All the yields are good. In addition to corroborating Wolff's description of this acid (A., 1902, i, 678), the authors have prepared the silver salt and the dianhydride.

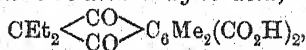
The acid has also been made, starting with 4:7-dimethyl-2:2-diethylhydrindene (*loc. cit.*), but this method is of no practical value. The hydrocarbon is condensed with acetyl chloride to form 5-acetyl-4:7-dimethyl-2:2-diethylhydrindene, a pale yellow oil, b. p. 150—160°/23 mm. (*semicarbazone*, m. p. 204—205°), and this is oxidised by fuming nitric acid.

II. *Higher Diethylindandione—Condensation Products of p-Xylene*.—When 4:7-dimethyl-2:2-diethylhydrindene and 4:7-dimethyl-2:2:5-triethylhydrindene are condensed with diethylmalonyl chloride, they yield the same product, 4:8-dimethyl-2:2:6:6-tetraethyl-*s*-benzdihydrinden-1:3-dione [4:8-dimethyl-2:2:6:6-tetraethyl-*s*-hydrindacene-1:3-dione] (annexed formula).

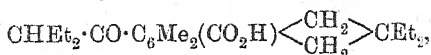


This forms mellitic acid on oxidation, which proves it to be a hexa-substituted derivative of benzene. The synthesis and reactions of the compound form the subject of this section.

4:7-Dimethyl-2:2:5-triethylindan-1:3-dione (above) is reduced by means of amalgamated zinc and hydrochloric acid to 4:7-dimethyl-2:2:5-triethylhydrindene, a petroleum-like oil, b. p. 163—164°/14 mm., D 0.916, n_D 1.51592. 4:8-Dimethyl-2:2:6:6-tetraethyl-*s*-hydrindacene-1:3-dione crystallises in leaflets, m. p. 103°, and may be reduced, as above, to 4:8-dimethyl-2:2:6:6-tetraethyl-*s*-hydrindacene, which forms elongated, rhombic leaflets, m. p. 69—71°. Both compounds yield mellitic acid on heating with pure nitric acid, but the diketone forms intermediately 4:7-dimethyl-2:2-diethylindan-1:3-dione-5:6-dicarboxylic acid,



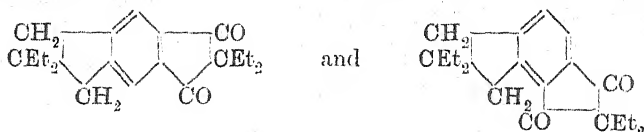
decomp. 315--320°, which shows that the reduced 5-ring is the weaker of the two in this case. When the diketone is boiled with concentrated potassium hydroxide, however, the other ring is ruptured in the usual way, the product being 6-*α*-ethylbutyryl-4:7-dimethyl-2:2-diethylhydrindene-5-carboxylic acid,



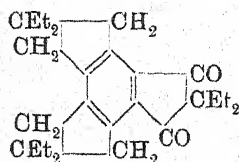
which crystallises in radiating filaments, m. p. 125°.

Attempts to prepare the 1:3:5:7-tetraketone corresponding with the above diketone by heating *p*-xylene with an excess of diethylmalonyl chloride in the presence of aluminium chloride were fruitless, the result merely being that a theoretical yield of 4:7-dimethyl-2:2-diethylindan-1:3-dione was obtained. This ketone itself could not be made to react further with diethylmalonyl chloride.

III. *Higher Diethylindandione—Condensation Products of Benzene.*—When 2:2-diethylindan-1:3-dione (from benzene and diethylmalonyl chloride) is reduced by Clemmensen's method, it forms 2:2-diethylhydrindene, as a pleasant-smelling oil, b. p. 118°/16 mm., $D_{20} 0.9162$, $n_D^{25} 1.5135$. This hydrocarbon condenses with diethylmalonyl chloride to form a mixture of 2:2:6:6-tetraethyls-hydrindacene-1:3-dione and 2:2:7:7-tetraethyl-as-hydrindacene-1:3-dione,



The mixture is a yellow, viscous oil, b. p. 221--238°/14 mm., which yields pyromellitic and mellophanic acids on oxidation with pure nitric acid, in the proportion of about 2:3. This indicates that the production of the unsymmetrical diketone is favoured. The mixture may be reduced by Clemmensen's method to the mixture of tetraethylhydrindacenes, m. p. 64°, b. p. 195--205°/26 mm., $D_{20} 0.941$, $n_D 1.5182$, only one of which, the unsymmetrical one, is capable of condensing with diethylmalonyl chloride to form a new indandione. This it does, and 2:2:5:5:8:8-hexaethylbenztri-hydrinden-1:3-dione, [1:3-diketo-2:2:5:5:8:8-hexaethyltrimethylenebenzene] (annexed formula) may be isolated from the product, in the form of glistening, hexagonal scales, m. p. 62--63°, which yield mellitic acid on oxidation.



IV. *A New Method for the Preparation of Pyromellitic Acid.*—2-Ethyl-*p*-xylene (section I., above) is condensed with acetyl chloride to form 2:5-dimethyl-4-ethylphenyl methyl ketone, m. p. 30--31°, b. p. 145--147°/19 mm., $D_{20} 0.9832$, $n_D^{20} 1.5352$, which yields a semicarbazone, in elongated, rhombic tablets, m. p. 173--174°. The ketone yields pyromellitic acid on

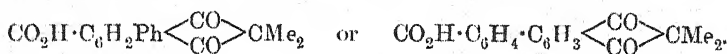
oxidation with pure nitric acid, but in one experiment a small amount of the intermediate product, 2:5-dimethylterephthalic acid, was obtained as well. On reduction, the ketone gives 1:4-dimethyl-2:5-dichylbenzene, which is a pleasant-smelling oil, b. p. 104.5—105°/15 mm., D^{20}_D 0.8803, n_D 1.5091.

V. *Indandiones from Dimethylmalonyl Chloride and Fluorene.*—When fluorene is condensed with dimethylmalonyl chloride, it yields at least three crystalline derivatives, which may be separated by fractional distillation, followed by crystallisations from benzene and alcohol. One of them is an *isobutyrylfluorene*

(*fluorenyl isopropyl ketone*), $\text{CH}_2 < \begin{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{CO} \cdot \text{CHMe}_2 \\ \text{C}_6\text{H}_4 \end{smallmatrix}$, m. p.

80—82°, the production of which is due to the rearrangement of the acyl chloride into *isobutyryl chloride*. The others are two of the three possible dimethylindandiones, but it is impossible to say which they are, as no polycarboxylic acids could be obtained on oxidation. α -*Fluorenedimethylindandione* [(α)-1:3-*Diketo-o-benzylene-2:2-dimethylhydrindene*], m. p. 220—221°, is sparingly soluble in alcohol; the β -compound, m. p. 156—158°, is freely soluble in the hot liquid. The mixture of the three ketones may be reduced by Clemmensen's method, and the products are more easy to separate. *isobutylfluorene* has m. p. 68—70°; α -*fluorenedimethylhydrindene* [(α)-*o-benzylene-2:2-dimethylhydrindene*] has m. p. 128—129°, and the β -isomeride has m. p. 135—137°. The two indandiones yield *fluorenedimethylindandiones* [1:3-*diketo-o-benzylene-2:2-dimethylhydrindenes*], $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} > \text{C}_6\text{H}_2 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{CMe}_2$,

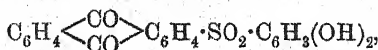
on oxidation with sodium dichromate and acetic acid; both α - and β -compounds have m. p. 263°, but the mixture melts at about 30° lower. The β -compound suffers hydrolysis and rupture of the typical benzylene ring on boiling with sodium hydroxide, the product being an *acid*, m. p. 237—238°, of the formula



J. C. W.

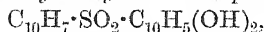
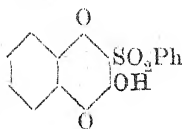
Dihydroxydiarylsulphones. O. HINSBERG (*Ber.*, 1917, 50, 953—958).—It has already been shown that aromatic sulphinic acids combine with *o*- and *p*-quinones and quinone-imines, provided that these contain no acidic or basic substituents, to form sulphones (*A.*, 1895, i, 144, 471; 1896, i, 684). Further applications of this reaction are now described.

Anthraquinone-2-sulphinic acid and benzoquinone yield 2:5-dihydroxyphenyl-2'-anthraquinonylsulphone,

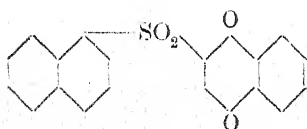


in yellow scales, m. p. 220°, which dissolve in sodium hydroxide with a green colour. Benzenesulphinic acid and 1:4-naphtha-

quinone form 1:4-dihydroxy-2-naphthylphenylsulphone, which separates in colourless crystals, m. p. 178°, and is oxidised by alkaline potassium ferricyanide to 3-hydroxy-2(1:4)-naphthaquinonylphenylsulphone (annexed formula), yellowish-green prisms, m. p. 214°. *p*-Benzoquinone and β -naphthalenesulphinic acid yield 2:5-dihydroxyphenyl-2'-naphthylsulphone, prisms, m. p. 216°, whilst α -naphthaquinone gives 1:4-dihydroxy-2:2'-dinaphthylsulphone,



leaflets, m. p. 174°. 2:5-Dihydroxyphenyl-1'-naphthylsulphone has m. p. 208°, and forms a dimethyl ether, m. p. 205°; 1:4-dihydroxy-



2:1'-dinaphthylsulphone has m. p. 191°, yields a diacetate, m. p. 222°, and is oxidised by chromic acid to 2(1:4)-naphthaquinonyl-1'-naphthylsulphone (annexed formula), yellow prisms, m. p. 227°. β -Naphthaquinone and α -naphthalenesulphinic acid yield 3:4-dihydroxy-1:1'-dinaphthylsulphone, m. p. 199°.

J. C. W.

Crystallisation of Menthol. FRED. E. WRIGHT (*J. Amer. Chem. Soc.*, 1917, **39**, 1515—1524).—Menthol crystallises in at least four different forms, of which only the α -form is stable between 0° and its m. p., 42.5°. The other three forms are monotropic, and melt respectively at 35.5° (β), 33.5° (γ), and 31.5° (δ). On account of the readiness with which the liquid may be undercooled, the three monotropic forms are easily obtained. The temperature of crystallisation appears to be the chief factor which determines the nature of the solid product. The unstable modifications are transformed into the α -form on keeping, but in this process the δ -modification may first pass into the β -form. All the forms of menthol show a pronounced tendency towards the development of radial spherulites. These are approximately spherical when the crystals are formed from the liquid fusion, but noticeably ellipsoidal when the α -crystals result from the transformation of the monotropic modifications.

H. M. D.

Volatile Constituents of Leaves of *Alpina nutans*, Roscoe. K. KAFUKU, *Kogyo-Kwagaku-Zasshi* (*J. Chem. Ind. Tokyo*, 1917, **20**, 349—353; from *J. Soc. Chem. Ind.*, 1917, **36**, 905).—The leaves of *Alpina nutans*, Roscoe, contain 0.053% of a volatile oil, D_{20}^{20} 0.9301, n_D^{20} 1.4750, α_D (100 mm.) + 38.4°; saponification value, 9.88; saponification value after acetylation, 36.1. The chief constituents of the oil are *d*-camphor (more than 30%) and *d*-camphane (17%). Other constituents are cineol and an ester of cinnamic acid, and probably limonene, a sesquiterpene, and a phenol of high boiling point.

T. S. P.

Optical Activity of Pine Species. D. E. TSAKALOTOS (*Gazzetta*, 1917, 47, i, 285—287).—Oil of turpentine from *Pinus halepensis* (Aleppo pine) has $[\alpha]_D +47-48^\circ$, whereas that from *P. maritima* has $[\alpha]_D -40.5^\circ$. Gildemeister's statement ("Die aetherischen Oele," Leipzig, 1913, II, 133) that Belloni obtained Aleppo pine-needle oils with $[\alpha]_D -22.355^\circ$ and -26.518° , is erroneous, these oils being obtained from *P. maritima*. Genuine Aleppo pine-needle oil consists largely of *d*-pinene, independently of the locality or of the season when it is distilled; a sample from Attica was found to have $[\alpha]_D +39.4^\circ$. T. H. P.

Products of Oxidation of Aloin. E. SEEL, C. KELBER, and W. SCHARF (*Ber.*, 1917, 50, 759—764).—By the oxidation of aloin in aqueous solution with Caro's acid, the authors have obtained a trihydroxymethylanthraquinone ("aloe-emodin," compare Seel, A., 1901, i, 92; *Süddeutsch. Apothekerzeitung*, 1906, 624), together with a red, crystalline tetrahydroxymethylanthraquinone, m. p. 193—195° (tetra-acetyl derivative, yellow, crystalline powder, m. p. 198—201°; tetra-benzoyl derivative, yellow, crystalline powder, m. p. 236—238°). The same tetrahydroxy-compound was formed in the oxidation of aloin with aqueous hydrogen peroxide. Hydrolysis of the acetyl and benzoyl derivatives gave rise to a substance of the composition of a tetrahydroxymethylanthraquinone, but of m. p. 232—234°. D. F. T.

Bixin. J. HERZIG and F. FALTIS (*Ber.*, 1917, 50, 927—929. Compare Heiduschka and Panzer, this vol., i, 408).—It is claimed that the real difficulty in determining the empirical formula of bixin lies in the fact that the combustion of the pigment requires special precautions. By observing these, results agreeing with $C_{26}H_{30}O_4$ are always obtained. J. C. W.

Uroerythrin. V. BORRIEN (*J. Pharm. Chim.*, 1917, [vii], 16, 45—51).—Uroerythrin may be readily obtained in alcoholic solution from urine by shaking it with powdered talc, collecting the sediment, washing it well with water, and extracting the solid residue with 95% alcohol alone or slightly acidified with hydrochloric acid. The brick-red sediments from certain urines also yield this pigment in a purer state if they are mixed with talc, washed with water, and extracted as above. Such alcoholic solutions, when exposed to light, rapidly lose their colour, the pigment being destroyed. From an alcoholic solution, kept in the dark, there is a slow deposition of the pigment on the walls of the containing vessel. The absorption spectrum of its alcoholic solution shows two bands, one at $\lambda=550-525$, and the other at $\lambda=510-484$. An alcoholic solution of uroerythrin gives with a few drops of dilute solutions of ammonium, sodium, or potassium hydroxide a greenish-blue coloration. Dilute acids give a pink coloration. The pigment probably exists in the urine in a colloidal state and its abundance is proportional to the amount of uric acid or urates contained in the urine. W. G.

The Mass Action of Water on Dyes. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1917, **39**, 1338—1348).—A large number of dyes are found to undergo colour changes on diluting largely with water. Sensitive solutions of this nature are obtained in some cases when the dye is mixed with only a trace of acid or alkali, but other dyes require relatively large quantities of acid or alkali to make sensitive solutions. Starting with an acid solution, if the colour has been changed by dilution, the addition of acid will restore the original shade, and similarly, alkalis will restore the colour of a changed alkaline dye. For example, a red, feebly alkaline solution of cochineal becomes blue on dilution, and red again on adding alkali; a fairly acid solution of methyl-violet changes from greenish-orange to green, blue, indigo, and finally violet; strongly alkaline solutions of picric acid change from red to yellow. A table showing the behaviour of some sixty-three dyes is given, but at least one hundred other dyes were found to be unaffected by dilution.

The common indicators suffer changes in colour by dilution only when the amount of acid or alkali present is very small. The most serviceable indicator is therefore one that is stable towards water in the presence of the smallest concentration of OH or H ions. No dyes give sensitive solutions in both alkaline and acidic media, and altogether it may be assumed that the effects are not due to ionisation, but to the mass action of the water in causing chromoisomerisation or some other change of the molecule.

The colours of the above dyes in pyrophosphoric acid solutions are also recorded. Basic dyes are found to be prevalingly red in pyrophosphoric acid, although many of them have other shades in concentrated aqueous solutions. In fact, it is more than probable that the colour exhibited in an aqueous solution is really that of the mixture of products formed by hydrolytic action. If the phosphoric acid solutions are diluted with water, the colour changes are in the order of the spectrum.

The mechanism of the hydrolysis of dyes is briefly discussed. As is generally recognised, the changes in molecular state which a dye may undergo may be due to (1) different colloidal forms, (2) polymerisation, (3) quinhydrone formation, (4) hydration, or (5) tautomerism, in all of which water may be operative. J. C. W.

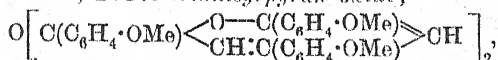
Pyrylium Compounds. II. WALTHER DILTHEY (*J. pr. Chem.*, 1917, [ii], **95**, 107—120. Compare A., 1916, i, 829).—Triphenylpyranol, the synthesis of which was described in the earlier paper, is an amphoteric substance capable of giving coloured salts with acids and also with alkalis, although the products of the latter class, which form yellowish-red solutions, are unstable and readily undergo fission with formation of benzoic acid and an unidentified oily compound. The presence of the hydroxyl group in triphenylpyranol can be proved by treatment with methyl iodide and sodium methoxide in methyl-alcoholic solution with formation of methoxy-2 : 4 : 6-triphenylpyran,

$$\text{CH} \begin{array}{c} \text{CPh} \text{---} \text{O} \\ \diagup \quad \diagdown \\ \text{CPh} \text{---} \text{CH} \end{array} \text{CPh} \text{---} \text{OMe},$$

tablets or prisms, m. p. 142—143° (corr.), insoluble in alcoholic potassium hydroxide. All other attempts to demonstrate the presence of the hydroxyl group proved fruitless, the pyranol compound in some cases proving refractory and in other cases undergoing decomposition. With hydrazine hydrate in pyridine solution, colourless needles, m. p. 123—125° (decomp.), were obtained of a substance (deep brown *picrate*, m. p. 166°, corr.), of which the constitutional formula probably is $\text{CPh} \begin{smallmatrix} \text{CH} \\ \text{CH} \end{smallmatrix} \begin{smallmatrix} \text{CPh} \\ \text{CPh} \end{smallmatrix} \text{N} \cdot \text{NH}_2$; this

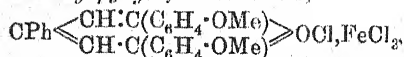
substance, unlike triphenylpyranol, failed to react with semicarbazide, and when heated above its m. p. gave rise to 2:4:6-triphenylpyridine. In the earlier publication the action of semicarbazide on triphenylpyranol has been shown to yield $\alpha\gamma\epsilon$ -triphenyl- Δ^{β} -penten- $\alpha\epsilon$ -dione disemicarbazone; the interaction of benzylidenediacetophenone and semicarbazide in pyridine solution forms a quite distinct substance, namely, the *disemicarbazone*, $\text{CHPh}(\text{CH}_2 \cdot \text{CPh} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2)_2$, prisms, m. p. 232—233° (corr.).

For the synthesis of the trianisylpyrylium complex, it was not possible to follow exactly the method employed for triphenylpyranol, and it was found necessary first to effect the condensation of anisaldehyde and *p*-methoxyacetophenone in the presence of alkali to the corresponding oily diketone, which, without being purified, was then heated with ferric chloride, acetic acid, and acetic anhydride. The resulting 2:4:6-trianisylpyryl ferrichloride, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{CH} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \\ \text{CH} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \end{smallmatrix} \text{OCl, FeCl}_3$, brownish-yellow needles, m. p. 271—272° (corr.), which in acetic acid, alcohol, or pyridine gives solutions with a greenish-yellow fluorescence, yields its pseudo-base on treatment with sodium carbonate solution, sodium acetate failing to produce this result. The pseudo-base in this case is not the simple pyranol compound, but its dehydration product, 2:4:6-trianisylpyran oxide,

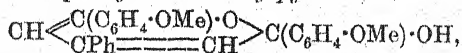


colourless needles, m. p. 84° (corr.), soluble in sulphuric acid with a greenish-yellow fluorescence; this, in ethereal solution with picric acid, formed red 2:4:6-trianisylpyryl *picrate*, m. p. 278—279° (corr.), dilute solutions of which exhibit a beautiful fluorescence.

4-Phenyl-2:6-dianisylpyryl ferrichloride,



prepared like the triphenylpyryl analogue by the interaction of *p*-methoxyacetophenone (2 mols.), benzaldehyde (1 mol.), and ferric chloride in hot acetic anhydride, forms brownish-red prisms, m. p. 265—266° (corr.), with a green glance, and gives solutions with a yellow fluorescence; on treatment with sodium carbonate, the ferrichloride yielded 4-phenyl-2:6-dianisylpyranol,



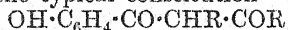
almost colourless needles, m. p. 106°, which gives a strongly

fluorescent solution in sulphuric acid, and in ethereal solution reacts with picric acid, forming *4-phenyl-2:6-dianisylpyryl picrate*, red needles, m. p. 272—273° (corr.). D. F. T.

The Crystalline Form of Maltol (Lariscinic Acid, 3-Hydroxy-2-methyl-1:4-pyrone). H. STEINMETZ (*Zeitsch. Kryst. Min.*, 1916, 55, 377—379).—Maltol exists in two modifications, an α -monoclinic and a β -rhombohedral form. By crystallisation from chloroform the α -variety alone is obtained, generally in the form of small, thin tables [$a:b:c=0.3977:1.04013$; $\beta=109^\circ 40'$]. From 50% alcohol solution the α - and β -forms are obtained together. The rhombic crystals of the latter have [$a:b:c=0.5490:1.05867$]. From the fact that, if crystals of the β -form are placed in a saturated chloroform solution they disappear and give place to the α -form, it is concluded that the α -form is the stable modification.

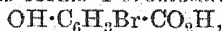
E. H. R.

The Hydrolysis of Chromones by Dilute Alkali. H. SIMONIS (*Ber.*, 1917, 50, 779—786).—The fission of the heterocyclic ring in the chromones by an approximately *N*-aqueous solution of sodium hydroxide occurs generally at the ether-oxygen atom, the primary product of the typical constitution



undergoing further decomposition, so that the final product is the corresponding salicylic acid derivative.

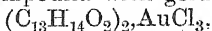
In the case of 2:3:5-trimethylchromone, it has already been observed that the action of alkali yielded an oily product without acidic character (Simonis and Lehmann, A., 1914, i, 424), and the assumption that this product was 2-hydroxy-6-tolyl ethyl ketone, $\text{OH}\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{COEt}$, is now confirmed, the substance having been obtained in a pure, crystalline condition, prisms, m. p. 28.5°. The abnormal course of the fission process with this substance is probably due to the influence of the methyl radicle in the 5-position, because the 2:3:6- and 2:3:8-trimethylchromones yield the corresponding salicylic acids, whilst 2:3:5:7-tetramethylchromone and 5-bromodimethylchromone give rise respectively to 5-hydroxy-4-methyl ethyl ketone, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}_2\cdot\text{COEt}$, colourless needles, m. p. 78°, and 6-bromo-2-hydroxyphenyl ethyl ketone, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{COEt}$, colourless prisms, m. p. 82°, although 7-bromodimethylchromone under similar conditions forms 4-bromosalicylic acid,



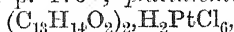
colourless needles, m. p. 212°; likewise, in the hydrolytic fission of 2:3:5:8-tetramethylchromone, no dimethylsalicylic acid is produced. The effect of a substituent in the 5-position therefore appears to be a general one. D. F. T.

2:3:5:7-Tetramethylchromone. H. SIMONIS and L. HEROVICI (*Ber.*, 1917, 50, 787—793. Compare Simonis, preceding abstract).—2:3:5:7-Tetramethylchromone, $\text{C}_6\text{H}_2\text{Me}_4$ $\begin{matrix} \text{CO}\cdot\text{CMe} \\ | \\ \text{O}\cdot\text{CMe} \end{matrix}$, needles, m. p. 100.5°, was obtained by the action of phosphoric

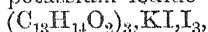
oxide on a mixture of methyl methylacetoacetate and *s*-xylenol containing a little alcohol. The chromone forms a *hydrochloride*, m. p. 106°; *hydrobromide*, m. p. 193°; *dibromide*, $C_{13}H_{14}O_2Br_2$, m. p. 182°; *oxime*, needles or hexagonal crystals, m. p. 196°; *mercurichloride*, $C_{13}H_{14}O_2 \cdot HgCl_2$, needles, m. p. 202—203°; *mercurichloride-hydrochloride*, $(C_{13}H_{14}O_2)_2 \cdot HgCl_2 \cdot HCl \cdot H_2O$, colourless crystals; *uranyl chloride-hydrochloride*, $(C_{13}H_{14}O_2)_2 \cdot UO_2Cl_2 \cdot 2HCl$, yellow solid; *additive compound with gold chloride*,



orange-yellow solid, m. p. 176°; *platinichloride*,



reddish-yellow solid, m. p. 202°; *ferrichloride-hydrochloride*, $(C_{13}H_{14}O_2)_3 \cdot FeCl_3 \cdot 2HCl$, yellow, crystalline solid, m. p. 150—152°; *additive compound with potassium iodide and iodine*,



bronzey needles, m. p. 79—81°.

By nitration in the cold with a mixture of sulphuric and fuming nitric acids, 6-nitrotetramethylchromone, $NO_2 \cdot C_6HMe_2$ $\begin{matrix} \swarrow CO \cdot CMe \\ \searrow O - CMe \end{matrix}$, colourless needles, m. p. 128—129°, was obtained, whilst treatment at 110° with phosphorus pentasulphide produced 2:3:5:7-tetramethyl-4-thiochromone, $C_6H_2Me_2$ $\begin{matrix} \swarrow CS \cdot CMe \\ \searrow O - CMe \end{matrix}$. D. F. T.

Decomposition of Quinine Hydrogen Sulphate. B. F. HOWARD and O. CHICK (*Pharm. J.*, 1917, **99**, 143—144).—The conditions have been ascertained under which quinine hydrogen sulphate is converted into quinicine and quinotoxin. The material containing 7H₂O decomposes to the extent of 0.25% at 60°, whilst, if previously dried at 35—40°, no decomposition occurs at this temperature. The addition of small quantities of water (for example, half its weight) at any dangerous temperature increases the decomposition, whilst larger quantities of water retard it. The limiting temperature at which quinine hydrogen sulphate, heated alone or in very concentrated solution, first decomposes is 60°. At 90°, 50% decomposes in twenty-four hours and 75% in forty-eight hours. In an open vessel the decomposition is only 17% in twenty-four hours owing to exsiccation. Melting the hydrated salt probably always causes decomposition. The formation of a bright yellow fusion giving a highly coloured, very refractive solution, is a certain indication of decomposition. The authors suggest the use of the dihydrochloride or the dihydrobromide for solutions which require sterilisation by heat. H. W.

A Synthesis of Tropinone. ROBERT ROBINSON (*T.*, 1917, **111**, 762—768).—The formula for tropinone suggests that the substance might, theoretically, be hydrolysed into succinaldehyde, methylamine, and acetone, and it has, in fact, been found possible to synthesise it by the interaction of these com-

pounds. The synthesis was also carried out by using ethyl acetone-dicarboxylate or calcium acetonedicarboxylate instead of acetone. In the last case, the succindialdehyde was mixed in water with acetonedicarboxylic acid, which was then neutralised by the addition of calcium carbonate, methylamine, in water, being afterwards gradually added, and the mixture allowed to remain at the ordinary temperature for fifty hours. On working the product up, tropinone, melting at 42° , was obtained in a yield of 42% of the theoretical. In these experiments, the dipiperonylidene derivative was used as a means of detecting the merest traces of tropinone. This substance is readily obtained by the condensation of tropinone with piperonal in alcoholic potassium hydroxide solution, and after crystallisation from ethyl acetate forms bright yellow needles melting at 214° , which are but sparingly soluble in most organic solvents. T. S. PA.

Yohimbine and Quebrachine. EDUARDO FILIPPI (*Arch. Farmacol. speriment.*, 1917, **23**, 107—128, 129—140; from *Chem. Zentr.*, 1917, i, 1019—1020).—From purely chemical evidence, Fourneau and Page (A., 1914, i, 862) have come to the conclusion that yohimbine and quebrachine are identical. [Contrast, however, Spiegel (A., 1916, i, 287).] The author has carried out a careful pharmacological comparison of the two alkaloids, from which he is drawn to the conclusion that although they are similar in many respects, yet in others they show such marked differences that they cannot be considered as identical, although belonging to the same pharmacological group.

The chemical similarity of the two alkaloids with each other and with strychnine is further shown by the occurrence of Vitali's reaction. H. W.

Silver Compound of the Acridine Series (Disinfectant), and a Process of Making Same. SOC. CHEM. IND. BASLE (U.S. Pat., 1227624, 1917; from *J. Soc. Chem. Ind.*, 1917, **36**, 905).—Compounds of value as disinfectants are obtained by the action of a soluble silver salt, in presence of a solvent, on acridine dyes which may be alkylated at the acridine nitrogen. Special claim is made for the silver compound of 3:6-diamino-2:7-dimethylacridine, methylated at the acridine nitrogen. It is a brownish-red powder, forming coloured solutions in water, alcohol, acetone, ethyl acetate, acetic acid, and sulphuric acid. It acts as a disinfectant in solutions of great dilution, strongly checking the growth of bacteria, especially streptococci and splenitis bacilli.

T. S. P.

Cadmium Compounds of the Acridine Series, and a Process of Making the Same. SOC. CHEM. IND. BASLE (U.S. Pat., 1228926, 1917; from *J. Soc. Chem. Ind.*, 1917, **36**, 867).—An acridine dye, alkylated at the acridine nitrogen, is heated with a soluble cadmium salt in presence of a solvent. The cadmium

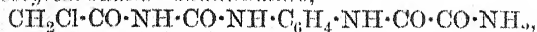
compound of 3:6-diamino-2:7-dimethylacridine, methylated at the acridine nitrogen, is specially claimed. T. S. P.

Unsymmetrical Derivatives of Aromatic Diamines.

WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1447—1465).—Derivatives of *m*- and *p*-phenylenediamines and 2:4-tolylenediamine are described. The chief contribution by the authors is a number of chloroacetyl derivatives (compare this vol., i, 552), but new details and improved methods of preparation are recorded in the case of several older compounds.

I. DERIVATIVES OF *m*-PHENYLENEDIAMINE.—*m*-Aminoacetanilide has m. p. 86·5—87·5° (corr.), and the hydrochloride forms transparent plates, m. p. 280°; *m*-chloroacetylaminooacetanilide crystallises in radiating masses of needles, m. p. 212—214° (decomp.). *m*-Acetylaminophenylcarbamide forms colourless aggregates of thin plates, m. p. 204—205·5° (decomp.); its hydrochloride is a feathery solid, m. p. above 275° (decomp.); *m*-aminophenylcarbamide crystallises in radiating groups of long, prismatic needles, m. p. 128—130° (corr.); *m*-chloroacetylaminophenylcarbamide forms delicate, matted needles, m. p. 192—193° (gas evolution). *m*-Aminophenylglycine (mentioned in D.R.-P., 96857) crystallises in pale brown wedges, m. p. 193—194° (decomp.); its methyl ester dihydrochloride (methyl *m*-aminoanilinoacetate dihydrochloride) forms rosettes of minute spears, decomp. 196—197°; *m*-aminoanilinoacetamide, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, crystallises in rosettes of flat needles, m. p. 145·5—146·5° (corr.).

m-Amino-oxanilic acid may be prepared by heating *m*-phenylenediamine with crystalline oxalic acid at 115—140°; it crystallises in masses of needles with $1\text{H}_2\text{O}$, m. p. 245° (decomp.), but cannot be converted into the amide. Ethyl *m*-nitro-oxanilate (from *m*-nitroaniline and ethyl oxalate at 160°) can be converted, however, into *m*-nitro-oxanilamide, m. p. 268—269° (effervescence), and this reduced by the ferrous sulphate and ammonia method to *m*-amino-oxanilamide, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$, thin, hexagonal plates, m. p. 191—191·5°. *m*-Chloroacetylaminooxanilamide forms masses of minute needles, decomp. 281°; *m*-carbamido-oxanilamide separates in voluminous, hair-like masses, decomp. above 260°; *m*-chloroacetylcarbamido-oxanilamide,



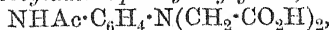
crystallises in rosettes of flat needles and platelets, decomp. 233—234°.

Ethyl *m*-nitromalonanilate, from *m*-nitroaniline and ethyl malonate at 200—210°, crystallises in delicate, cream-coloured needles, m. p. 73·5—74°; *m*-nitromalonanilide has m. p. 198—200° (corr.); *m*-aminomalonanilide, $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$, forms glistening, creamy needles, m. p. 180·5° (corr.).

II. DERIVATIVES OF *p*-PHENYLENEDIAMINE.—*p*-Chloroacetylaminooacetanilide forms minute prisms, decomp. 265—270°. *p*-Acetylaminophenylcarbamide yields chloroacetyl-*p*-acetylaminophenyl-

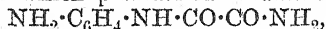
carbamide, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$, in lenticular platelets, m. p. 235—237° (decomp.). *p*-Aminophenylcarbamide forms flat, glistening needles or long platelets, and melts at 162—164° with evolution of gas, then resolidifies and remains solid at 285°; *p*-chloroacetylaminophenylcarbamide crystallises in aggregates of flat needles, m. p. 225° (evolution of gas; resolidification).

p-Aminoacetanilide, when boiled with sodium chloroacetate solution, yields *p*-acetylaminophenyldiglycine,



in sheaves of needles, m. p. 234—235° (effervescence), whilst with ethyl chloroacetate it gives *ethyl p*-acetylaminophenyglycine (*ethyl p*-acetylaminooanilinoacetate), in rosettes of long, slender needles, m. p. 124—125° (corr.). This ester is hydrolysed by boiling hydrochloric acid to *p*-aminophenyglycine, m. p. 222—223° (decomp.) (compare D.R.-P., 88433); the ester dihydrochloride of this (*ethyl p*-aminoanilinoacetate dihydrochloride) has m. p. 201—202° (decomp.), and yields *p*-aminophenyglycineamide (*p*-aminoanilinoacetamide), m. p. 161—164°, when treated with aqueous ammonia.

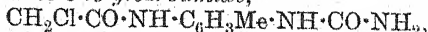
p-Amino-oxanilic acid yields *p*-chloroacetyl-amino-oxanilic acid, as a mass of microscopic needles, decomp. 235°. *Methyl p*-amino-oxanilate crystallises in greenish-yellow, silky needles, m. p. 129—130° (corr.), and forms a *hydrochloride*, long, thin, pale purple plates, from which *p*-amino-oxanilamide,



a pale purple, microcrystalline powder, m. p. 217—218°, may be prepared, and converted into *p*-chloroacetyl-amino-oxanilamide, which is not molten at 280°.

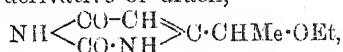
p-Nitromalonanilide forms flat, brownish-yellow needles, m. p. 241—242° (decomp.); *ethyl p*-nitromalonanilate crystallises in pale yellow, slender needles or platelets, m. p. 92—95°; *p*-nitromalonanilamide forms yellow, rhombic platelets, m. p. 218—220° (decomp.); *p*-aminomalonanilamide crystallises with $1\text{H}_2\text{O}$, and melts partly at 200—210°; *p*-chloroacetylaminomalonanilamide, $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, forms sheaves of slender filaments, m. p. 243—244° (decomp.).

III. DERIVATIVES OF 2:4-TOLYLENEDIAMINE.—4-Acetyl-amino-*o*-toluidine hydrochloride, decomp. 263—264°, yields 4-acetyl-amino-2-chloroacetylaminotoluene [*2*-chloroacetylaminoocto-*p*-toluidide] in felted masses, m. p. 230—231° (decomp.). 5-Acetyl-amino-2-methylphenylcarbamide [*4*-acetyl-amino-*o*-tolylcarbamide] crystallises in felted needles, m. p. 240° (effervescence; resolidification), and is hydrolysed by means of hydrochloric acid to 4-amino-*o*-tolylcarbamide, which forms stellate groups of spikes, m. p. 199—200°, and yields a *hydrochloride*, sheaves of minute needles, and also 4-chloroacetyl-amino-*o*-tolylcarbamide,



radiating masses of delicate needles, m. p. 224—225° (evolution of gas).

Pyrimidines. LXXXIV. Transformation by Hydrolysis of Secondary Pyrimidine Nucleosides into Iminazole Combinations. TREAT B. JOHNSON and SIDNEY E. HADLEY (*J. Amer. Chem. Soc.*, 1917, **39**, 1715—1717).—The crystalline compound, $C_5H_8ON_2$, obtained by hydrolysing the ethyl ether of the secondary alcohol derivative of uracil,



by means of aqueous hydrobromic acid (compare Johnson and Hadley, A., 1916, i, 754), is now found to be identical with 4:5-dimethylglyoxalone (compare Biltz, A., 1908, i, 56); its diacetyl compound was prepared. T. H. P.

Ring Formation with the Elimination of a Nitro-group. S. REICH and (MLE.) B. TURKUS (*Bull. Soc. chim.*, 1917, [iv], **21**, 107—111).—6-Chloro- and 6-bromo-2-nitrobenzaldehydephenylhydrazone, like the corresponding 2:6-dinitro-compound (compare A., 1913, i, 995), when warmed with alcoholic potassium hydroxide lose their nitro-group and yield *isoidazoles*.

6-Bromo-2-nitrotoluene when heated in a sealed tube at 140° for six hours with bromine and magnesium carbonate yields 6-bromo-2-nitrobenzyl bromide, $NO_2 \cdot C_6H_3Br \cdot CH_2Br$, colourless needles, m. p. $71-72^\circ$, which when warmed in alcoholic solution with aniline gives 6-bromo-2-nitrobenzylaniline, red crystals, m. p. 105° . This compound, when oxidised in acetone solution with potassium permanganate, yields 6-bromo-2-nitrobenzylideneaniline, an oil which on hydrolysis gives 6-bromo-2-nitrobenzaldehyde, m. p. 82° . This aldehyde gives a *phenylhydrazone*, occurring in two forms, (1) red needles, m. p. 146° , (2) yellow needles, m. p. 142° , which are readily converted the one into the other. This hydrazone when warmed with alcoholic potassium hydroxide on a water-bath gives 4-bromo-1-phenylisoidazole, $C_6H_3Br \begin{array}{c} \diagup CH \\ \diagdown NPh \end{array} > N$, pale yellow crystals, m. p. 98° . Similarly, 6-bromo-2-nitrobenzaldehyde- β -naphthylhydrazone, m. p. 192° , gives 4-bromo-1- β -naphthylisoidazole, m. p. 135° .

6-Chloro-2-nitrobenzaldehydephenylhydrazone forms red needles, m. p. 161° , and gives 4-chloro-1-phenylisoidazole, m. p. 84° .

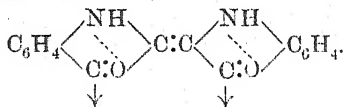
6-Chloro-2-nitrobenzaldehyde- β -naphthylhydrazone yields yellow needles, m. p. 178° , and gives 4-chloro-1- β -naphthylisoidazole, yellow needles, m. p. 112° . W. G.

Ring Formation with the Elimination of a Nitro-group. S. REICH (*Bull. Soc. chim.*, 1917, [iv], **21**, 111—114. Compare preceding abstract).—2:4-Dinitrobenzaldehydephenylhydrazone, unlike its 2:6-isomeride (compare A., 1913, i, 995), does not undergo ring formation in the presence of potassium hydroxide. The influence in these cases is probably steric, since ethyl 2:4-dinitrophenylglyoxylate phenylhydrazone yields the corresponding *isoidazole*. This view is supported by the fact that 2:4-dinitro-

acetophenonephenylhydrazone readily undergoes ring formation and 2:4:6-trinitrobenzaldehydephenylhydrazone readily yields 5:7-dinitro-1-phenylisindazole, red needles, m. p. 148°. W. G.

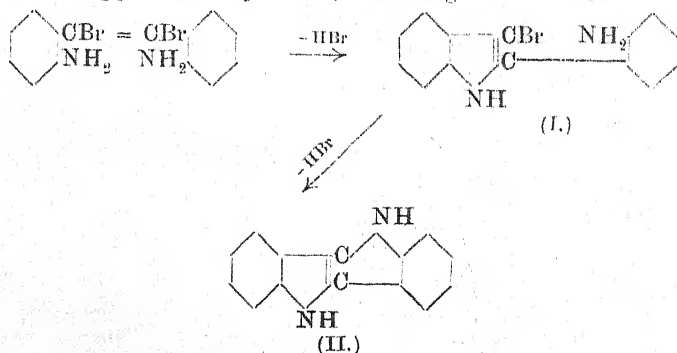
The Indigo Chromophore. I. LIFSCHITZ and HEINRICH LOURIE (*Ber.*, 1917, **50**, 897—906).—The absorption spectra of indigotin, "dithioindigo," and Claasz's compounds, "mono-sulphurylindigo" ["sulphurylindoxyl- α -indolindigo," *A.*, 1916, i, 753] and "disulphurylindigo" ["sulphurylindigo," *ibid.*, 842], have been determined, in suitable organic solvents and in concentrated sulphuric acid. The usual curves are reproduced.

Attention is directed to the phenomenon of halochromism in the indigo series. Indigotin itself gives an olive-green solution in sulphuric acid and a bluish-green in a mixture of chloroform and stannic chloride; "dithioindigo" is emerald-green in sulphuric acid and violet in the foregoing mixture, and the whole alteration of the absorption spectra in sulphuric acid resembles that suffered by halochromic $\alpha\beta$ -unsaturated ketones. The peculiar feature of the true indigoid chromophore is the intimate connexion between the carbonyl group and the imino-group (or sulphur atom), as Claasz has rightly emphasised (*ibid.*, 841). For ordinary chemical purposes, the authors are in agreement with Claasz's formulæ, but in optical considerations they prefer one with residual affinities, as below, in order to explain the halochromism, rather than a formula with rigid bonds.



J. C. W.

Formation of a Doubly Condensed Indole. PAUL RUGGLI (*Ber.*, 1917, **50**, 883—893).—The author describes a double application of Lipp's indole synthesis, according to the scheme:



A contraction of di-indole, namely, "dindole," is proposed as a name for the compound II. Systems of this type are known in the pyrrole series, but not in the indole group.

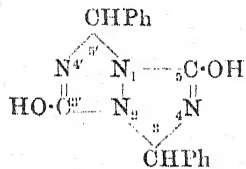
$\alpha\alpha$ -Dibromo-2:2'-dinitrostilbene (Pfeiffer, A., 1912, i, 619) is reduced by means of stannous chloride dissolved in a solution of hydrogen chloride in glacial acetic acid to $\alpha\alpha$ -dibromo-2:2'-diaminostilbene, which forms colourless leaflets, and suffers brisk decomposition at 168—169° when quickly heated, but undergoes rearrangement at about 125—140°, when slowly heated, into a compound with m. p. 260°. One molecule of hydrogen bromide is readily removed from this by boiling for a short time with alcoholic picric acid. 3-Bromo-2-o-aminophenylindole (I) crystallises in colourless bundles of needles, m. p. 146—147°, and may be reduced by means of sodium amalgam to the known 2-o-aminophenylindole (A., 1911, i, 433). The removal of the second portion of hydrogen bromide requires prolonged boiling with alcoholic potassium hydroxide. Dindole (II) crystallises from anisole or nitrobenzene in very pale yellow, rhombic crystals, m. p. 320—325° (decomp.).

The closing of the indole ring by means of picric acid solutions can also be effected in the case of the conversion of 2:2'-diaminotolane into 2-o-aminophenylindole, but not in the case of 2:2'-diaminostilbene, probably owing to the fact that the *dipicrate* of this (brown crystals with violet reflex, decomp. 209°) is so sparingly soluble.

J. C. W.

The Criss-cross Addition on Conjugate Systems. The Action of Cyanic Acid, Thiocyanic Acid, and *iso*Cyanates on Azines. J. R. BAILEY and A. T. McPHERSON (*J. Amer. Chem. Soc.*, 1917, 39, 1322—1338).—In a recent paper (this vol., i, 355)

it was shown that benzaldazine combines directly with two molecules of cyanic acid. Arguments are now advanced in support of the view that the product has the proposed structure, namely, that of a "5:3'-dihydroxy-3:5'-diphenyldihydro-1:2-triazolotriazole" (annexed formula). This being so, the reaction implies the simultaneous attachment of



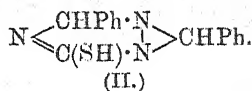
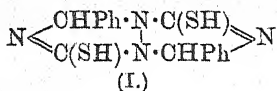
atomic complexes at the 1:3- and 2:4-positions of a conjugated system of double linkings, or a "criss-cross" addition. Similar results are obtained in the cases of thiocyanic acid and phenylcarbimide, and the azines of benzaldehyde, *m*-nitrobenzaldehyde, cinnamaldehyde, and furfuraldehyde.

Benzaldazine and phenylcarbimide react at 160—170° to form "5:3'-diketo-3:4:4':5'-tetraphenylhexahydro-1:2-triazolotriazole," which crystallises in rhombohedral plates, m. p. 263° (decomposing into phenylcarbimide and benzaldazine, and subsequently nitrogen and stilbene), and yields benzaldehydephenylcarbamylhydrazone, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$, as a mass of interlacing needles, m. p. 180°, when heated with potassium hydroxide (1:1) at 130°. The hydrazone may be reduced by means of sodium amalgam in boiling alcohol to α -phenylcarbamyl- β -benzylhydrazine, prisms, m. p. 138°, oxidised by heating with alcoholic ferric chloride at 130° to 5-hydroxy-3:4-diphenyltriazole, a mass of long, interwoven needles,

m. p. 260°, and hydrolysed by sulphuric acid to benzaldehyde and phenylsemicarbazide, $\text{NHPH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, m. p. 128°.

Other azines react with phenylcarbimide as follows: *m*-nitrobenzaldazine yields "5:3'-diketo-4:4'-diphenyl-3:5'-di-*m*-nitrophenylhexahydro-1:2-triazolotriazole," m. p. 260° (decomp.); cinnamaldazine gives "5:3'-diketo-4:4'-diphenyl-3:5'-distyrylhexahydro-1:2-triazolotriazole," m. p. 243° (decomp.); and furfuraldazine forms "5:3'-diketo-4:4'-diphenyl-3:5'-difurylhexahydro-1:2-triazolotriazole," m. p. 257° (decomp.).

Cinnamaldazine and furfuraldazine also combine with cyanic acid (potassium cyanate in glacial acetic acid) to form "5:3'-dihydroxy-3:5'-distyryldihydro-1:2-triazolotriazole," m. p. 192° (decomp.), and "5:3'-dihydroxy-3:5'-difuryldihydro-1:2-triazolotriazole," m. p. 191°, respectively. Using potassium thiocyanate and glacial acetic acid, "5:3'-dithiol-3:5'-difuryldihydro-1:2-triazolotriazole," decomp. 154—156°, and "5:3'-dithiol-3:5'-diphenyldihydro-1:2-triazolotriazole" (I), thin, rhombic plates, m. p. 187° (decomp.), may be prepared. The latter forms a sparingly soluble, orange-yellow compound with mercuric chloride (1:1), and is converted into 5-thiol-3-phenyl-1:2-benzylidenc-triazole (II), slender prisms, m. p. 166°, when heated with concentrated potassium hydroxide at 150°.



J. C. W.

Methyl- and Ethyl-uric Acids. EINAR BJELMAN and JOHANNE BJERRUM (*Ber.*, 1917, 50, 837—847. Compare this vol., i, 177; Biltz and Heyn, this vol., i, 292).—The authors have already shown that of the so-called α -, δ -, and ζ -isomerides of 3-methyluric acid, the last two are identical, and by a re-examination of the results of Biltz and Heyn (*loc. cit.*), who have demonstrated that the α -acid contains 3-methyluric acid mixed with some 9-methyluric acid, they are now able to produce evidence that " α -3-methyluric acid" in reality is a molecular compound of 3-methyl- and 9-methyl-uric acids. The evidence is based on concurrent chemical and crystallographic investigation of the " α -acid" and of mixtures of the 3-methyl- and 9-methyl-isomerides in varying proportions. The solubility of the " α -acid" in water exceeds the combined values for the 3-methyl acid and the 9-methyl acid, so that in aqueous solution it must largely retain its bimolecular condition; on the other hand, freezing-point determinations with the " α -acid" and its constituents in alkaline solution indicate that under these conditions the complex molecule of the former acid is almost entirely resolved into a molecule of the 3-methyl acid and one of the 9-methyl acid.

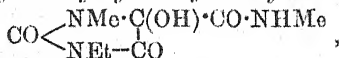
The ethyluric acid known hitherto contains the substituent radicle in the 7- or 9-position; on treating uric acid with ethyl iodide and excess of potassium hydroxide in aqueous solution, a

crystalline 3-ethyluric acid is obtained, which can also be formed synthetically by the stages ethyl acetoacetate, methyluracil, potassium nitrouracilcarboxylate, potassium nitrouracil, nitroethyluracil, ethylisobarbituric acid, ethylisodialuric acid, and ethyluric acid. The presence of the ethyl group in the six-membered ring is confirmed by oxidation of the acid to *diethylalloxantin*, rhombic leaflets, the 3-position being indicated from analogy to the 3-methyluric acid prepared in a similar manner. D. F. T.

Derivatives of Trimethyl-9-ethyluric Acid. HEINRICH BILTZ and MARGARETE BERGIUS (*Annalen*, 1917, 414, 54—67. Compare this vol., i, 286—300).—A study of the reactions of tetra-alkyluric acids is of especial interest because the triketonic configuration is the only one possible in them. The behaviour of tetramethyluric acid (*loc. cit.*, 299) is now found to be shared by other tetra-alkyl derivatives.

Caffeine is converted into 8-chloro- and then into 8-ethoxycaffeine, and this is heated at 240° in a sealed tube with a little alcohol, when it changes into 1:3:7-trimethyl-9-ethyluric acid. This acid is accompanied by trimethyluric acid, which is removed by neutralisation with barium hydroxide, the tetra-derivative being extracted from the dried material by means of chloroform. Pure trimethyl-9-ethyluric acid crystallises in aggregates of thin, monoclinic leaflets, m. p. 203—204°, and distils with partial decomposition and liberation of ethylene at about 370°.

When treated with chlorine and methyl alcohol in the cold, the acid yields 4:5-dimethoxy-1:3:7-trimethyl-9-ethyl-4:5-dihydrouric acid, which crystallises in monosymmetric, limpid tablets, m. p. 97·5°, whilst the less stable 4:5-diethoxy-derivative, m. p. 142°, is formed in ethyl alcohol. These ethers yield the parent trimethyl-ethyluric acid on heating with hydriodic acid, and 1:7-dimethyl-3-ethylcaffolide,
$$\begin{array}{c} \text{NMe}\cdot\text{CO} > \text{C} < \begin{array}{c} \text{NMe}\cdot\text{CO} \\ \text{CO}-\text{NEt} \end{array} \\ \text{CO}-\text{O} \end{array}$$
 m. p. 102°, when boiled with dilute hydrochloric acid. The same product is easily obtained by the action of chlorine on the tetra-alkyluric acid in cold water. The caffolide is hydrolysed by prolonged boiling with water to 5-hydroxy-1-methyl-3-ethylhydantoinylmethylamide,



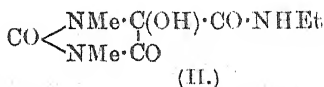
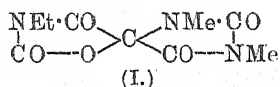
m. p. 140°, and yields 1-methyl-3-ethylhydantoinylmethylamide, m. p. 185°, b. p. 220—230°, on reduction with hydriodic acid.

When a suspension of trimethylethyluric acid in glacial acetic acid is treated with chlorine, 1:7:9-trimethyl-3-ethylspiro-5:5-dihydantoin,
$$\begin{array}{c} \text{NMe}\cdot\text{CO} > \text{C} < \begin{array}{c} \text{NMe}\cdot\text{CO} \\ \text{CO}-\text{NEt} \end{array} \\ \text{CO}\cdot\text{NMe} \end{array}$$
 is obtained, in monoclinic tablets, m. p. 99·5°. J. C. W.

Trimethyl-1-ethyluric Acid and its Derivatives. HEINRICH BILTZ and FRITZ MAX (*Annalen*, 1917, 414, 68—78).—Theobromine is converted into 1-ethyl-, 8-chloro-1-ethyl-, and then

8-methoxy-1-ethyl-theobromine, which crystallises in very slender needles, m. p. 164—165°, and this is transformed by heating at 170° into 3:7:9-trimethyl-1-ethyluric acid, rhombic tablets, m. p. 176—177°. 4:5-Dimethoxy-3:7:9-trimethyl-1-ethyl-4:5-dihydrouic acid, m. p. 95°, and the corresponding diethoxy-compound, m. p. 105°, are obtained by the action of chlorine in the presence of the appropriate alcohol, and 1:7:9-trimethyl-3-ethylspiro-5:5-dihydantoin (see preceding abstract) by the action of chlorine in glacial acetic acid.

1:3-Dimethyl-7-ethylcaffolide (I), m. p. 93°, is formed when the tetra-alkyluric acid is treated with chlorine and water, or when the above ethers are boiled with dilute hydrochloric acid, and this is hydrolysed by boiling with water to 5-hydroxy-1:3-dimethyl-hydantiolethylamide (II), m. p. 153°:



The latter compound may be reduced by hydriodic acid to 1:3-dimethylhydantiolethylamide, m. p. 196°, b. p. 290° (decomp.), oxidised by chromic acid to dimethylparabanic acid, or hydrolysed by means of barium hydroxide to ethylamine, mesoxalic acid, and dimethylcarbamide. J. C. W.

3:7-Dimethyl-1:9-diethyluric Acid and its Derivatives.

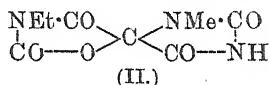
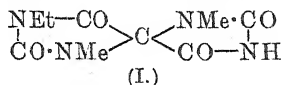
HEINRICH BILTZ and FRITZ MAX (*Annalen*, 1917, **414**, 79—84).—8-Chloro-1-ethyltheobromine is converted into 8-ethoxy-1-ethyltheobromine, a cotton-wool-like mass of needles, m. p. 153—154°, and this is transformed, by heating at 230° in a sealed tube, into 3:7-dimethyl-1:9-diethyluric acid, which crystallises in monoclinic tablets, m. p. 158°. 4:5-Dimethoxy-3:7-dimethyl-1:9-diethyl-4:5-dihydrouic acid, small rhombohedra, m. p. 78°, and 1:9-dimethyl-3:7-diethylspiro-5:5-dihydantoin, prisms, m. p. 120°, are obtained in the usual way. 1-Methyl-3:7-diethylcaffolide is likely to be a solid of low melting point, but no crystalline product could be obtained by the action of chlorine and water on the tetra-alkyluric acid. The diethoxy-compound was also not obtained, for under the usual conditions the product was the above spirodihydantoin. The latter is hydrolysed by barium hydroxide to 3:8-dimethyl-1:6-diethylallantoin, which crystallises in bundles of slender prisms, m. p. 124°. J. C. W.

Derivatives and Degradation of 3:7-Dimethyl-1-ethyluric Acid. HEINRICH BILTZ and FRITZ MAX (*Annalen*, 1917, **414**, 85—98).—This acid was briefly described by E. Fischer (A., 1883, 357), but it has now been examined more thoroughly along the lines of the present research into the alkyluric acids.

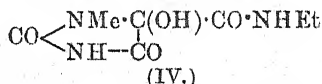
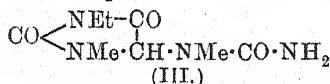
The acid, m. p. 345°, may be obtained by hydrolysing 8-ethoxy-1-ethyltheobromine (preceding abstract). It reacts with alcohol and chlorine to form 4:5-diethoxy-3:7-dimethyl-1-ethyl-4:5-dihydrouic acid (Fischer's "diethoxyhydroxyethyltheobromine"). The corre-

sponding 4:5-dimethoxy-3:7-dimethyl-1-ethyl-4:5-dihydrouric acid, rhombohedra, m. p. 178°, can be obtained in the same manner, or more conveniently from 1-ethyltheobromine by the action of chlorine and methyl alcohol. As it is easily reduced to 3:7-dimethyl-1-ethyluric acid by means of stannous chloride, this acid is best prepared by that method.

The authors confirm Fischer's statement that 3:7-dimethyl-1-ethyluric acid yields methylamine, 1:9-dimethyl-3-ethylspiro-5:5-dihydantoin ("hypoethyltheobromine") (I), m. p. 142°, and



1-methyl-7-ethylcaffolide ("apoethyltheobromine") (II), m. p. 138°, when a solution in concentrated hydrochloric acid is saturated with chlorine at -10° and then evaporated. The spiro-compound is best obtained by the action of alcoholic hydrogen chloride on the above ethers, and the caffolide by the action of chlorine and water on 3:7-dimethyl-1-ethyluric acid. The crude, concentrated solution of 1:9-dimethyl-3-ethylspiro-5:5-dihydantoin yields 1:6-dimethyl-3-ethylallantoin (III), in bundles of long needles, when warmed with barium hydroxide, whilst 1-methyl-7-ethylcaffolide changes into 5-hydroxy-1-methylhydantoyl-ethylamide (IV), bundles of slender prisms, m. p. 167°, when boiled with water for some time:



If 3:7-dimethyl-1-ethyluric acid is shaken with glacial acetic acid and chlorine, it yields 5-chloro-3:7-dimethyl-1-ethyl- $\Delta^{4:9}$ -isouric acid,

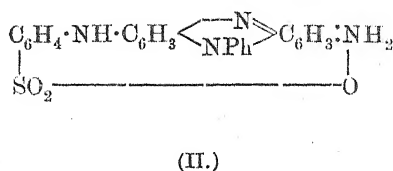
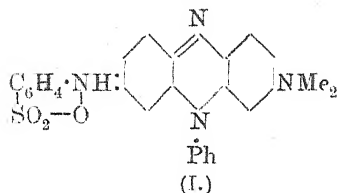
$\begin{array}{c} \text{NEt}\cdot\text{CO}\cdot\text{CCl}\cdot\text{NMe} \\ | \\ \text{CO}\cdot\text{NMe}\cdot\text{C}\cdot\text{N}\cdot\text{CO} \end{array}$, in slender prisms, m. p. about 150° (decomp.). This may be reduced by stannous chloride to the parent acid or converted into the above diethyl ether by means of alcohol.

3:7-Dimethyl-1-ethyluric acid has also been submitted to the usual oxidative degradation, and converted into s-dimethyldiethylalloxantin, $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_4\cdot 2\text{H}_2\text{O}$, hexagonal leaflets or needles, m. p. 174°; methylethylalloxan, $\text{C}_7\text{H}_8\text{O}_4\text{N}_2\cdot \text{H}_2\text{O}$, rhombic tablets (anhydride, m. p. 124°); and methylethylvioluric acid, $\text{C}_7\text{H}_9\text{O}_4\text{N}_3\cdot \text{H}_2\text{O}$, elongated tablets from water, long, hexagonal tablets, m. p. 95–96°, from alcohol (potassium salt, reddish-violet with $2\text{H}_2\text{O}$, violet-blue when anhydrous). J. C. W.

Monosulphonic Acids of Quinone-imide Dyes. F. KEHRMANN and ALEXANDER HERZBAUM (*Ber.*, 1917, 50, 873–882).—It frequently happens in the dye works laboratory that attempts are made to convert sparingly soluble dyes, especially basic ones, into soluble, acid dyes for wool by sulphonating them, and the usual experience is that one sulphonic acid residue is not sufficient to achieve the desired effect. No explanation of this fact seems to

have been offered, but the obvious suggestion is now made that the monosulphonic acids are internal salts. A number of them are described.

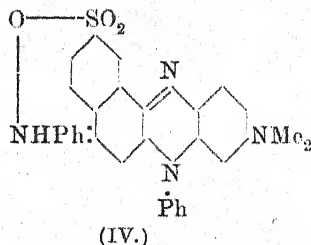
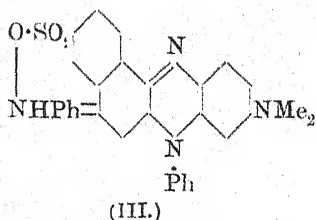
Indazinesulphonic acid (I) is obtained by warming the base with ten times its weight of concentrated sulphuric acid. It crystall-



lises in metallic-brown leaflets, gives a green solution in sulphuric acid, which becomes blue and finally violet on dilution, forms a salt in alcoholic potassium hydroxide, but not in aqueous alkali, dyes tanned cotton a good violet shade in warm, dilute acetic acid, and yields sulphanilic acid when heated with hydrochloric acid at 160°.

Phenylphenosafraninesulphonic acid (II) is obtained by oxidising together *p*-phenylenediamine and diphenyl-*m*-phenylenediamine in acetic acid solution with chromic acid, and dissolving the product (*ψ*-mauveine acetate) in warm sulphuric acid. It crystallises as a reddish-brown, metallic powder, partly with 1H₂O; it gives a blue solution in alcoholic potassium hydroxide, which becomes violet on diluting, the insoluble dye being reprecipitated.

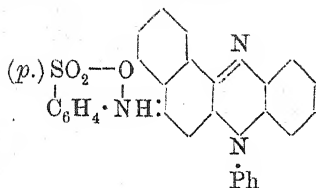
Naphthindazine-8-sulphonic acid (III) (D.R.-P., 78497) is formed by warming together 1:3-dianilinonaphthalene-7-sulphonic acid, *p*-nitrosodimethylaniline hydrochloride, and sodium acetate in alcohol. It forms brown, metallic crystals, gives a *potassium* salt, which dissolves with reddish-violet colour in water or alcohol, but not in dilute potassium hydroxide, and it scarcely colours tanned cotton. *Naphthindazine-9-sulphonic acid* (IV) is very much like the



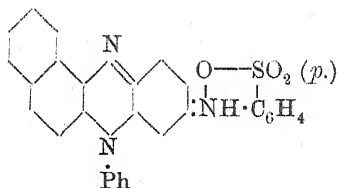
isomeride; it is prepared by condensing *p*-nitrosodimethylaniline with 1:3-dianilinonaphthalene-6-sulphonic acid (from *α*-naphthylamine-3:6-disulphonic acid and aniline).

Phenylrosindulinesulphonic acid (V) (patented by the Badische Co.) dissolves readily in dilute alkali hydroxides or ammonia, but not in alkali carbonates. It is an inner anhydride, which retains

1H₂O even at 185°. *Phenylisrosindulinesulphonic acid* (VI) resembles the isomeride, except in being blue.

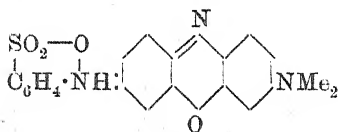


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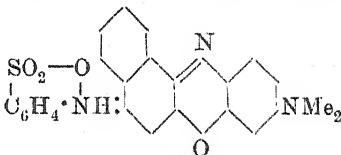


(VI.)

Nitrosodiphenylamine and *m*-dimethylaminophenol give an azoxine dye which dissolves in warm sulphuric acid to form the *sulphonic acid* (VII), which crystallises in bluish-green, brassy needles, with 1H₂O. It gives violet salts in alkali hydroxide solutions, but not with carbonates, and dyes tanned cotton pale greenish-blue. Phenyl-Nile-blue, from *p*-nitroso-*m*-dimethylamino-

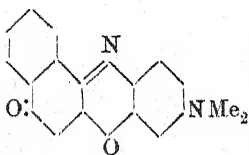


(VII.)



(VIII.)

phenol and 1-anilinonaphthalene (Nietzki and Bossi, A., 1893, i, 44), forms the *sulphonic acid* (VIII) in metallic-green crystals, with 1H₂O, which give reddish-brown salts with alkali metals, which are insoluble in excess of alkali hydroxide or carbonate. The sulphonation is slow and incomplete, as some of the acid decomposes into *dimethylaminophenonaphthazoxone* (annexed formula). This crystallises from chloroform (the sulphonic acid is insoluble) in large, steely leaflets, m. p. 248—250°. The colours of the solutions and the fluorescence of this compound vary with the refractive index of the solvent, but in the opposite sense to Kundt's rule. The bluish-red



solution in alcohol exhibits fiery-red fluorescence; the red, chloroform solution fluoresces yellowish-red; and the orange-red solution in a mixture of ether, benzene, and carbon disulphide has greenish-yellow fluorescence.

J. C. W.

Constitution and Colour. V. The Colour of Azocompounds and their Salts. II. F. KEHRMANN and STANISLAS HEMPEL (*Ber.*, 1917, 50, 856—872. Compare A., 1916, i, 165).—The absorption spectra, both in the visible and ultra-violet regions, have been determined for azobenzene, *p*-aminoazobenzene, *p*-dimethylaminoazobenzene, *pp'*-diaminoazobenzene, and *pp'*-tetramethyldiaminoazobenzene, in alcohol, acetic acid, alcoholic hydrogen chloride, and concentrated and fuming sulphuric acids. The

results are reproduced by the usual curves, and are discussed in some detail. The authors believe that they are sufficient to show that it is unnecessary to introduce the notion of quinone formation to explain the production of differently coloured salts of aminoazo-compounds. These salts can be regarded as containing different numbers of acid molecules attached to their nitrogen atoms.

J. C. W.

Chromoisomerism of Methyl-orange. WILLIAM M. DEHN and LOIS McBRIDE (*J. Amer. Chem. Soc.*, 1917, **39**, 1348—1377).—A large amount of experimental evidence, mostly of a simple and easily reproducible kind, has been gathered together in proof of the following points. (1) Methyl-orange or helianthin exists in a red, quinonoid form and a yellow, azoid form (compare Hantzsch, A., 1915, i, 322). (2) Aqueous solutions contain the two isomerides in equilibrium. Increased concentration, rise of temperature, or the addition of acids favours the red form; dilution, cooling or the addition of alkali disturbs the equilibrium in the direction of the yellow form. (3) Solutions in absolute phenol contain approximately 100% of the red isomeride; solutions in dry pyridine contain nearly 100% of the azoid form. Compared with these as standards, ordinary aqueous solutions contain 70—99% of the azoid form, even if they are acid, alkaline, or neutral. At great dilutions, helianthin salts, whether of acids or alkalis, are more or less pure yellow; that is, the mass effect of water is to yield the azoid form, regardless of the ionisation of the dye itself. In concentrated solutions, acid salts of helianthin are deep yellowish-red, alkaline salts, light reddish-yellow, that is, both quinonoid and azoid forms are present in each case.

The chief data recorded in this paper are those of the colorimetric comparison of solutions in phenol and pyridine as standards with those in 90% formic acid, *N*-hydrochloric acid, and water, alone or with various acids and bases. The original should be consulted by those engaged in similar studies, but the following facts of general interest may be mentioned. In *N*-hydrochloric acid solutions, on an average 87% of the dye has the azoid configuration, that is, the strong acid is capable of transforming only a small percentage of molecules into the quinonoid type. Pure helianthin averages about 97.7% of azoid molecules in water. In the presence of 1, 10, and 100 molecular proportions of sodium hydroxide, the azoid concentrations are 98.28, 98.59, and 98.67% respectively; that is, even much strong alkali does not give pure yellow solutions. Some of each chromoisomeride is present in any aqueous solution, and, therefore, in view of the disturbing influence of water on the equilibria, the concentration of the dye should be maintained constant in all accurate titrations.

J. C. W.

Colorimetric Determination of the Solubilities of Helianthin and its Salts. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1917, **39**, 1377—1381).—The solubility of helianthin in some acids, phenols, bases, alcohols, esters, aldehydes, ketones, ethers,

hydrocarbons, and other organic media, water, and saturated solutions of salt and sugars, has been determined by diluting 1 c.c. portions of the solutions to 250 c.c. with *N*-hydrochloric acid and matching the colour against standard solutions of pure helianthin in *N*-HCl. Helianthin is insoluble in hydrocarbons and their halogen, nitro-, and alkyloxy-derivatives; it forms soluble, red salts with certain acids and yellow salts with certain bases, but it also gives alternately red or yellow solutions in "indifferent" solvents, provided these contain chemically active groups (aldehyde or ketone) or labile hydrogen atoms. Even "indifferent" solvents have chemical action on helianthin, just as water has in changing the quinonoid into the azoid form. Possibly they combine with the amino- or sulphonic groups in helianthin, and so lead to one or other of the tautomeric forms.

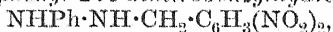
J. C. W.

Comparison of Phenylhydrazine Oxalate with Mesoxalic Acid Phenylhydrazone. W. L. EVANS, W. L. MONG, and F. L. SINKS (*J. Amer. Chem. Soc.*, 1917, **39**, 1724—1727).—New conditions are described for the preparation and analysis of phenylhydrazine oxalate, with which the compound described by Causse (A., 1894, i, 569) as mesoxalic acid phenylhydrazone is shown to be identical.

Basic bismuth mesoxalate, $\text{Bi(OH)(C}_3\text{O}_5)_2 \cdot 2\text{H}_2\text{O}$, prepared by a method similar to that used by Vanino and Zumbusch (A., 1909, ii, 56) for obtaining normal bismuth oxalate, forms a white precipitate. When treated with hydrogen sulphide, and the product thus obtained with phenylhydrazine, it yields mesoxalic phenylhydrazone, whereas Vanino and Zumbusch's normal oxalate and Causse's bismuth mesoxalate (*loc. cit.*) yield phenylhydrazine oxalate under similar conditions.

T. H. P.

Phenyl-2:6-dinitrobenzylhydrazine. S. REICH (*Bull. Soc. chim.*, 1917, [iv], **21**, 114—117).—[With G. GAIGAILIAN and P. CHASKELIS].—2:6-Dinitrobenzyl bromide when boiled in alcoholic solution with phenylhydrazine, yields *as-phenyl-2:6-dinitrobenzylhydrazine*, $\text{NH}_2 \cdot \text{NPh} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, red crystals, m. p. 106—107°, and *s-phenyl-2:6-dinitrobenzylhydrazine*,



a viscid, red oil. The latter compound does not undergo ring-formation in the presence of alcoholic potassium hydroxide, but on exposure to air is oxidised to 2:6-dinitrobenzaldehydephenylhydrazone. The solid unsymmetrical hydrazine gives with nitrous acid *phenyl-2:6-dinitrobenzylnitrosoamine*, $\text{NO} \cdot \text{NPh} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, m. p. 116°, and with pyruvic acid it yields *pyruvic acid phenyl-2:6-dinitrobenzylhydrazone*, pale pink needles, m. p. 145—146°.

W. G.

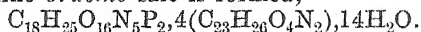
Picryl Azide. ERNST SCHRADER (*Ber.*, 1917, **50**, 777—778).—Picryl azide can be conveniently prepared by the interaction of picryl chloride and sodium azide in aqueous-alcoholic solution. The pure substance forms yellow prisms, m. p. 93° (compare Purgotti,

A., 1895, i, 27), and when heated with benzene or xylene loses a molecular proportion of nitrogen with the formation of 2:4-dinitro-1:6-dinitrosobenzene. It is only feebly explosive. D. F. T.

Tritico-Nucleic Acid. B. E. READ and W. E. TOTTINGHAM (*J. Biol. Chem.*, 1917, **31**, 295—301).—Tritico-nucleic acid prepared from the wheat embryo yields on hydrolysis the same products as yeast-nucleic acid (compare Jones and Read, this vol., i, 232, 233). Since in all its other properties tritico-nucleic acid closely resembles yeast-nucleic acid, it is probable that these two substances are really identical. H. W. B.

Uracil-Cytosine-Dinucleotide. WALTER JONES and B. E. READ (*J. Biol. Chem.*, 1917, **31**, 39—45. Compare this vol., i, 233).—When yeast-nucleic acid is heated with dilute sulphuric acid, its central nucleotide linking is not disturbed, but the two terminal nucleotide linkings are broken and *uracil-cytosine-dinucleotide* is formed. The dinucleotide, $C_{18}H_{25}O_{16}N_5P_2$, is obtained as a white, granular powder, $[\alpha]_D + 15.0^\circ$. On boiling with dilute sulphuric acid, it is slowly decomposed into its constituent pyrimidines, phosphoric acid, and carbohydrate. The decomposition is hastened by employing 25% sulphuric acid and heating in an autoclave at 140° ; indeed, this constitutes a good and quick method for the preparation of cytosine and uracil. On heating in an autoclave with 2% ammonium hydroxide at 140° , the dinucleotide yields uridine and cytidine.

On treatment of the dinucleotide with brucine in alcoholic solution, a crystalline *brucine* salt is formed,



It is obtained in needles which sinter at 170° and melt at 175° . The same conduct is exhibited by the brucine salt of adenine-uracil-dinucleotide, and is apparently a brucine phenomenon, as it occurs at the melting point of brucine (175°). H. W. B.

Guanine-Mononucleotide (Guanylic Acid) and its Preparation from Yeast-Nucleic Acid. B. E. READ (*J. Biol. Chem.*, 1917, **31**, 47—53).—When yeast-nucleic acid is heated with 2.5% ammonium hydroxide in an autoclave at 115° , the ammonium salt of guanine-mononucleotide is formed, and is readily separated by precipitation with alcohol. The lead salt is then formed by dissolving in water, acidifying with acetic acid, and treating with lead acetate. The free mononucleotide is afterwards liberated by hydrogen sulphide, and on concentration of the filtrate is obtained as a white, amorphous powder, $[\alpha]_D - 2.4^\circ$. It forms a *brucine* salt, $C_{10}H_{14}O_8N_5P, 2(C_{23}H_{26}O_4N_2), 7H_2O$, m. p. 203° , which on keeping in a vacuum desiccator over sulphuric acid rapidly loses water, which is slowly taken up again on exposure to the air. The substance readily parts with its phosphoric acid on warming with dilute sulphuric acid, like other purine-nucleotides.

Specimens of guanylic acid prepared from the pancreas of the

pig or the ox have properties which are identical with those of guanine-mononucleotide from yeast-nucleic acid. H. W. B.

Structure of the Purine Mononucleotides. WALTER JONES and B. E. READ (*J. Biol. Chem.*, 1917, **31**, 337—342. Compare this vol., i, 232).—On hydrolysis with dilute sulphuric acid, guanine mononucleotide liberates guanine with much greater rapidity than it liberates phosphoric acid. The mononucleotide must therefore have the structure $C_5H_4ON_5 \cdot C_5H_8O_3 \cdot O \cdot PO(OH)_2$, and not the alternative $C_5H_9O_4 \cdot C_5H_3ON_5 \cdot PO(OH)_2$. Adenine-uracil-dinucleotide similarly liberates its adenine far more rapidly than it liberates its phosphoric acid. As the two phosphoric acid groups of the dinucleotide are not directly joined to one another (compare Jones and Read, this vol., i, 233), it follows that adenine mononucleotide must also have a similar structure to that of the guanine mononucleotide. H. W. B.

The Absorption of Light by Oxyhæmoglobin. PAUL HÁRI (*Biochem. Zeitsch.*, 1917, **82**, 229—281).—A detailed investigation of the absorption of light of various wave-lengths by solutions of oxyhæmoglobin, and a comparison of the results obtained by previous investigators, chiefly Butterfield and Hüfner. S. B. S.

Enzyme Action. XV. Factors Influencing the Proteolytic Activity of Papain. EDWARD M. FRANKEL (*J. Biol. Chem.*, 1917, **31**, 201—215).—Commercial papain can be purified by precipitating the aqueous suspension of the powder with acetone or alcohol. The purified enzyme exerts its optimum action in a medium of which the hydrogen-ion concentration is 10^{-5} . Its activity is inhibited by both acids and alkalis, the latter being less destructive.

Papain resembles other enzymes in forming an intermediate compound with its substrate, which is subsequently broken up into the cleavage products with the liberation of unchanged enzyme. In the presence of hydrocyanic acid, the proteolytic action is intensified (compare Mendel and Blood, A., 1910, i, 796), and apparently the intermediate compound formed contains hydrocyanic acid, as well as papain and substrate. In the second stage of the action, the cleavage products are liberated, whilst both the hydrocyanic acid and the enzyme may be recovered almost quantitatively from the digestion mixtures. H. W. B.

Influence of Certain Electrolytes on the Course of the Hydrolysis of Starch by Malt Amylase. H. C. SHERMAN and JENNIE A. WALKER (*J. Amer. Chem. Soc.*, 1917, **39**, 1476—1493).—Having already determined the concentrations of hydrochloric acid, phosphoric acid, or potassium dihydrogen phosphate, which favour optimum activity of purified malt amylase (A., 1915, i, 183), the authors have been able to study the rate of formation of reducing sugar from soluble starch under various conditions.

The saccharogenic action of the enzyme is found to be increased by the addition of the optimum amounts of electrolytes, not only in the early stages, but throughout. The greater the concentration of enzyme, the less is the benefit derived from the electrolytes; with 0.0012% of the enzyme acting on a 1% solution of starch, the hydrolysis is as rapid and complete without electrolytes as with.

When more than the optimum amount of acid is added, the hydrolysis proceeds at a slower rate than the best throughout. This inhibitory effect is most marked with hydrochloric acid, less with phosphoric, and least with potassium dihydrogen phosphate. Probably, owing to secondary ionisation, the optimum H-ion concentration is maintained in the latter cases ("buffer effect"). With less than the optimum amount of electrolyte, the original speed of hydrolysis is sustained better than with too much electrolyte.

Up to the point at which half the theoretical amount of sugar has been formed, provided that favourable amounts of electrolyte are present, the speed of hydrolysis is proportional to the concentration of starch and of enzyme. There seems to be no region in which the yield of sugar is directly proportional to time, nor is there any cessation of hydrolysis or establishment of an equilibrium when 80% of the possible yield is obtained, as some have supposed. Even the comparatively resistant dextrins which remain towards the end are attacked, but at a very slow rate. J. C. W.

A Noteworthy Effect of Bromides on the Action of Malt Amylase. ARTHUR W. THOMAS (*J. Amer. Chem. Soc.*, 1917, **39**, 1501—1503).—Whereas the chlorides, nitrates, sulphates, and phosphates of sodium and potassium activate purified malt amylase in proportion to their concentrations (A., 1915, i, 183), the bromides exert an inhibitory effect when present in small amounts, but an activating influence in greater concentrations. J. C. W.

Enzyme Action. XIV. Further Experiments on Lipolytic Actions. K. GEORGE FALK (*J. Biol. Chem.*, 1917, **31**, 97—123. Compare Falk and Sugiura, A., 1915, i, 92).—From a study of the numerous ways in which inactivation of lipase and esterase may be accomplished, the author is led to suggest that the activity of these enzymes is associated with the presence of the grouping —C(OH):N— , and that inactivation occurs when this grouping is converted into the tautomeric —CO·NH— structure. In support of this hypothesis, it is found that dipeptides containing the above specified grouping exert a distinct hydrolytic action on ethyl butyrate and glyceryl triacetate, and that the addition of alkali, which presumably favours the production of the enolic tautomeride, is accompanied by a distinct increase in the hydrolytic power of the dipeptide. The author demonstrates by means of control experiments that it is not the increased alkalinity of the solutions which is chiefly responsible for the increased hydrolysis. It is also noted that equimolecular quantities of different

dipeptides produce the same amount of hydrolysis of glyceryl triacetate in the same time.

The simple amino-acids, which do not contain the $-\text{C}(\text{OH})\cdot\text{N}-$ grouping, exert a relatively small hydrolytic action on glyceryl triacetate and ethyl butyrate. Comparison of the hydrolytic effects produced by an amino-acid and the corresponding dipeptide renders it possible to assign a definite hydrolytic value to the $-\text{C}(\text{OH})\cdot\text{N}-$ grouping, which is the same, within limits, no matter from which pair of related substances the value is calculated.

Substances containing the $-\text{C}(\text{OR})\cdot\text{N}-$ grouping, such as ethyl iminobenzoate, $\text{C}_6\text{H}_5\cdot\text{C}(\text{NH})\cdot\text{OEt}$, resemble the naturally occurring lipases in that a maximum hydrolytic action is obtained at a definite hydrogen-ion concentration, and that the activity disappears when the substance is changed by the action of acids or alkalis, or by heating or even prolonged keeping in solution.

Partial hydrolysis of proteins probably produces substances possessing the $-\text{C}(\text{OH})\cdot\text{N}-$ grouping, and the author notes that proteins treated with alkalis exert marked hydrolytic action on esters, even after the free alkali has been removed by neutralisation or dialysis.

H. W. B.

Metallic Derivatives of Diaminodihydroxyarsenobenzene.

J. DANYSZ (Eng. Pat., 104496; from *J. Soc. Chem. Ind.*, 1917, **36**, 906).—The compounds obtained from 3:3'-diamino-4:4'-dihydroxyarsenobenzene and mercury salts are difficult to use therapeutically, since they are only slightly soluble in dilute acids and decompose when sodium hydroxide is added. If, however, they are treated with antimony compounds, antimonyl derivatives are obtained which are more soluble, stable in alkaline solution, more active, and less toxic.

T. S. P.

Metallic Derivatives of Diaminodihydroxyarsenobenzene.

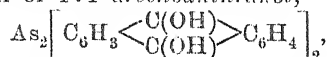
J. DANYSZ (Brit. Pat., 104497; from *J. Soc. Chem. Ind.*, 1917, **36**, 907).—One mol. of 3:3'-diamino-4:4'-dihydroxyarsenobenzene hydrochloride is treated in aqueous solution with 1 mol. of a freshly prepared silver haloid, and 1 mol. of antimony trichloride is dissolved in the solution by heating; to the resulting solution is added a concentrated solution of citric acid; dilute sulphuric acid is then added to precipitate the base. The silver salt may be replaced by the salts of gold, platinum, or copper. The stable products obtained are much more antiseptic and relatively less toxic than the parent substance.

T. S. P.

Arsenic Compounds of the Anthraquinone Group.

L. BENDA (*J. pr. Chem.*, 1917, [ii], **95**, 74—106).— α -Aminoanthraquinone, by diazotisation in concentrated sulphuric acid, was converted into the corresponding diazo-compound, which on treatment with a solution of sodium arsenite in the presence of sodium carbonate, gave rise to colourless *anthraquinone-1-arsinic acid*,

$C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} C_6H_3 \cdot AsO_3H_2$, colourless needles. This substance is reduced by sodium hyposulphite in alkaline aqueous solution at 50° with formation of 1:1'-*arsenanthranol*,



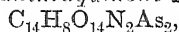
a deep brownish-red substance, which gives yellow solutions in alcohol and ether, but a blood-red solution in aqueous sodium hydroxide; when exposed to the atmosphere this alkaline solution undergoes rapid oxidation with re-formation of the arsenic acid, but in the presence of sodium carbonate, atmospheric oxidation of the arsenanthranol proceeds only to yellow *anthraquinone-1-arsenoxide*, $C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} C_6H_3 \cdot AsO$, for the further oxidation of which to anthraquinonearsinic acid hydrogen peroxide is necessary. Anthraquinone-1-arsinic acid, when heated strongly, undergoes decomposition with formation of erythrohydroxyanthraquinone, $C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} C_6H_3 \cdot OH$, arsenious oxide and water; on reduction with sodium amalgam in alkaline solution, it undergoes fission into anthraquinone and arsenious acid, the ease of this change probably accounting for the high toxicity of the arsenic acids of the anthraquinone group.

Anthraquinone-2-arsinic acid, prepared by a similar process to that adopted for its 1-isomeride, forms yellow needles, which remain unfused at 270° ; like the 1-compound, it gives precipitates with calcium chloride and with magnesia mixture in ammoniacal solution at the ordinary temperature. Anthraquinone-2-arsinic acid is relatively resistant to the action of sodium amalgam and aqueous alkali, this behaviour being in accord with the fact that it is much less poisonous than the isomeric 1-arsinic acid.

4-Aminoanthraquinone-1-arsinic acid, $C_{14}H_{10}O_6NaAs$ (sodium salt, red needles with $4H_2O$), was obtained as a red, crystalline powder, m. p. indistinct at 278° (decomp.), by the interaction of an alkaline solution of sodium arsenite with the product formed on diazotising 1:4-diaminoanthraquinone in diluted sulphuric acid. The product of diazotisation in concentrated sulphuric acid, using an excess of nitrosylsulphuric acid, reacted with sodium arsenite, forming *4-hydroxyanthraquinone-1-arsinic acid*, $C_{14}H_9O_6As$, yellow needles, decomp. above 200° (sodium salt, brownish-yellow needles); this yielded a brownish-red precipitate with magnesia mixture at the ordinary temperature, and in solution in sulphuric acid could be nitrated to *3-nitro-4-hydroxyanthraquinone-1-arsinic acid*, $C_{14}H_8O_6NaAs$, yellow needles, decomp. near 230° , the constitution of which was demonstrated by reduction with ferrous hydroxide to aminohydroxyanthraquinone, m. p. near 250° , and conversion of this into alizarin by heating with hydrochloric acid at 250° . Reduction of 3-nitro-4-hydroxyanthraquinone-1-arsinic acid with a restricted quantity of ferrous hydroxide yielded *3-amino-4-hydroxyanthraquinone-1-arsinic acid*, $C_{14}H_{10}O_6NaAs$, violet, silky needles, m. p. near 265° , the arsenic-containing radicle escaping elimination

under these conditions. The product formed a *hydrochloride* and gave a crystalline *diazo*-compound (needles), which coupled with *R*-salt and with resorcinol, producing violet- and blue-coloured solutions respectively; it was also reducible by sodium hyposulphite to an orange-coloured vat, which imparted a violet stain to filter-paper.

1:5-Diaminoanthrarufin was converted by way of its chocolate-brown, crystalline tetrazo-compound into 4:8-*dihydroxyanthraquinone*-1:5-*diarsinic acid* (*anthrarufindiarsinic acid*), $C_{14}H_{10}O_{10}As_2$, a yellow, microcrystalline powder, decomp. above 270° , the violet-coloured *disodium* salt of which gave in aqueous sodium hydroxide an orange-coloured solution presumably of the *tetrasodium* salt. On nitration in sulphuric acid at 80° this arsinic acid yielded 3:7-*dinitro*-4:8-*dihydroxyanthraquinone*-1:5-*diarsinic acid*,



a greenish-yellow, microcrystalline powder, the violet *disodium* salt of which, on successive treatment in solution with aqueous sodium hydroxide and alcohol, formed a bluish-red precipitate, presumably of the *tetrasodium* derivative. By treatment in alkaline aqueous solution with sodium amalgam, the dinitro-diarsinic acid was reducible to 3:7-*diamino*-4:8-*dihydroxyanthraquinone*-1:5-*diarsinic acid*, $C_{14}H_{12}O_{10}N_2As_2$, a dark violet powder with metallic reflex; *disodium* salt, crystalline with a coppery lustre.

D. F. T.

Physiological Chemistry.

The Hydrogen Number and Oxygen-combining Power of the Blood. K. A. HASSELBALCH (*Biochem. Zeitsch.*, 1917, 82, 282—288).—The constant k of Hill's formula, $y/100 = kx^{2.5}/1 + kx^{2.5}$, where y = % of complete saturation and x = oxygen tension, was determined with varying p_H for different bloods, the p_H being determined by the method recently described by the author (the estimation of free and bound carbon dioxide in the blood). If $-\log k$ is plotted on the ordinates and p_H on abscissa, a straight line is obtained, which in normal cases is the same as that obtained by Barcroft and Peters with the blood of Barcroft, that is, in normal cases, a given reaction of the blood corresponds with a definite value of the constant k . This does not hold, however, for certain pathological cases, and for this reason Barcroft's method of determining the reaction by estimation of the oxygen-combining capacity will not always give the correct results. S. B. S.

Uric Acid Content of the Blood of New-born Children. F. B. KINGSBURY and J. P. SEDGWICK (*J. Biol. Chem.*, 1917, 31, 261—268).—There is a striking parallelism between the high uric

acid content of the blood and of the urine of new-born children. This supports the view that the human fetal tissues are devoid of uricolytic power (compare Wells and Corper, A., 1909, ii, 749).

H. W. B.

The Assumed Destruction of Trypsin by Pepsin and Acid. III. Observations on Men. J. H. LONG and MARY HULL (*J. Amer. Chem. Soc.*, 1917, **39**, 1493—1500. Compare this vol., i, 361).—Experiments on men confirm the results obtained with dogs, that trypsin may resist the action of pepsin and acid for a considerable period in the stomach, even when the conditions are by no means abnormal. The plan of the work was as follows. A test meal was given, and after a time the stomach-content was drawn off by a tube and examined for acid, pepsin, bile, and possible tryptic action. If the conditions appeared to be normal, trypsin was fed with the meal and the stomach-content examined again. Tryptic activity was measured by the ability of the liquid to digest fibrin in a slightly alkaline medium, the factor recorded being the result of a formaldehyde amino-acid titration. If bile were found in the stomach, it would naturally suggest that trypsin had also been carried back by the regurgitation of duodenal fluid, but even when no bile was present the tryptic activity, due to the ingested ferment, was quite well marked, provided the acidity was not too great.

J. C. W.

Influence of Bile on the Production of Phenol. HARRY DUBIN (*J. Biol. Chem.*, 1917, **31**, 255—259. Compare A., 1916, i, 695).—By means of surgical procedures, it is possible to prevent the flow of bile into the small intestine. In the case of two dogs, an anastomosis was produced between the bile duct and the ureter, so that the bile passed directly into the urine. In another case an external bile fistula was produced, whereby it was possible to collect the bile so that the urine was free from it. It is found that, in these circumstances, large amounts of phenol are produced, unaccompanied by any increase in the conjugated acids. The increased production of phenol is due probably to the increased decomposition of the intestinal contents brought about by the diminished digestive activity caused by the absence of bile from the intestine. There is also a diminished inhibition of bacterial fermentative secretions. The unchanged conjugation indicates impaired liver function, or slow production of the phenol, or a combination of both.

H. W. B.

Hydrogen-ion Concentration of the Contents of the Ileum. J. F. McCLENDON, A. SHEDLOV, and W. THOMSON (*J. Biol. Chem.*, 1917, **31**, 269—270. Compare McCleendon, A., 1915, i, 915).—In pups, the contents of the ileum are slightly acid throughout the nursing period and, later, on a diet of solid food. The acidity ($p_H=6.3$) is less than the acidity of the contents of the duodenum in children during the first few days after birth ($p_H=3.1$).

H. W. B.

Metabolism of Sulphur. II. Influence of Small Amounts of Cystine on the Balance of Nitrogen in Dogs maintained on a Low Protein Diet. HOWARD B. LEWIS (*J. Biol. Chem.*, 1917, **31**, 363—377).—The addition of small amounts of cystine to the food of dogs on a low protein diet diminishes the loss of nitrogen from the body, and thus favourably influences the nitrogen balance. This is interpreted to be the result of a specific demand for the sulphur-containing cystine for metabolic purposes, since tyrosine and glycine added to the diet under similar conditions of experimentation do not diminish the loss of nitrogen or influence the state of nitrogenous equilibrium. H. W. B.

Calcium and Magnesium Metabolism. I. Effects of Alkali and Acid. MAURICE H. GIVENS and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1917, **31**, 421—433).—The addition of acids or alkalis to the food of dogs does not produce any significant change in the balance of nitrogen, calcium, magnesium, or phosphorus in the dog. The administration of hydrochloric acid increases the amount of calcium excreted in the urine at the expense of that excreted in the feces; the relation of calcium to magnesium in the urine is thereby changed. The calcium in milk is retained more readily by the body than the calcium in calcium lactate. In diabetes, the administration of large doses of alkali hydrogen carbonate does not decrease the output of calcium in the urine. H. W. B.

Calcium and Magnesium Metabolism. II. Effect of Diets Poor in Calcium. III. Effect of Fat and Fatty Acid Derivatives. MAURICE H. GIVENS (*J. Biol. Chem.*, 1917, **31**, 435—439, 441—444).—A definite relation between the output of calcium and nitrogen in dogs does not exist, and even when the diet is poor in calcium salts, storage of calcium does not occur, the calcium balance being negative. When the fat in the diet escapes absorption, the output of calcium is also increased, due to excretion of insoluble calcium soaps in the feces. Large quantities of fatty acids in the diet likewise occasion a loss of calcium from the body. H. W. B.

Comparative Metabolism of certain Aromatic Acids. CARL P. SHERWIN (*J. Biol. Chem.*, 1917, **31**, 307—310).—Phenylacetic acid administered to a monkey (*Macacus rhesus*) reappears in the urine in combination with glycine as phenylaceturic acid. The same change occurs after feeding dogs, rabbits, horses, and other lower animals with the substance. In the case of man, ingested phenylacetic acid is excreted partly as phenylacetylglutamine and partly as phenylacetylglutamine-carbamide (Thierfelder and Sherwin, A., 1915, i, 481). The monkey, therefore, is to be classed with the other lower animals rather than with man when judged from the point of view of the metabolic treatment of ingested phenylacetic acid. H. W. B.

Rôle of Vitamines in the Diet. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1917, **31**, 149—163).—The addition of 1.5%

of dried yeast to a diet of purified caseinogen, starch, lard, butter-fat, and artificial protein-free milk greatly increases its power to produce growth in rats. When, however, caseinogen is replaced by edestin, lactalbumin, or a vegetable protein, young rats fail to grow, although adult rats can be maintained in health over long periods. These results are surprising, especially in the case of lactalbumin, which has been shown to be capable of producing normal growth when present in comparatively small proportion in the diet (A., 1916, i, 690). Rats growing on the diet containing yeast and caseinogen cease to thrive immediately the yeast is withdrawn.

Experiments are described the results of which show that the rapidity of growth is related to the amount of yeast added to the food. In general, a proportion of 1.5% to 2% of yeast in the food is sufficient to produce normal growth. The yeast appears to have a direct action on the processes of growth and does not merely stimulate appetite. It is the improvement in the general condition of the animal caused by the addition of yeast to the diet which leads to the increase in the appetite.

The concentrated aqueous extract of yeast possesses the same stimulating capacity on the growth of rats as the yeast itself. These experiments confirm the presence in yeast of the so-called water-soluble vitamine (McCollum and Kennedy, A., 1916, i, 451).

H. W. B.

Vitamine Hypothesis and Deficiency Diseases. Experimental Scurvy. E. V. McCOLLUM and W. PITZ (*J. Biol. Chem.*, 1917, 31, 229—253).—The authors describe experiments in which guinea-pigs are fed on a diet which, although adequate to maintain rats in good health for indefinite periods, leads to the development of scurvy in these animals. These results are attributed, not to the absence of a specific protective substance or anti-scorbutic vitamine, but to a retention of faeces in the caecum owing to the unfavourable physical character of the diet, and to a consequent debility of the digestive tract through stretching and contact with irritating and toxic putrefaction products of bacterial origin. The addition to the diet of substances which depress the growth of micro-organisms in the digestive tract, such as sodium benzoate or citric acid, or which facilitate the elimination of the faeces, such as liquid petroleum, phenolphthalein, or orange juice, appears to prevent the development of scurvy; and, further, animals in which the scorbutic condition has been allowed to become pronounced are cured by the addition of these substances to the original diet.

The results are graphically illustrated by charts. H. W. B.

Nutrition Investigations on Cotton-seed Meal. III. Cotton-seed Flour. The Nature of its Growth-promoting Substances, and a Study in Protein Minimum. ANNA E. RICHARDSON and HELEN S. GREEN (*J. Biol. Chem.*, 1917, 31, 379—388. Compare this vol., i, 524).—Rats are fed on a diet of caseinogen, lard, starch, and mineral matter, together with varying

amounts of the aqueous and ethereal extracts of cotton-seed flour. Normal growth is attained when the amount of water-soluble accessory substance added to the food is equivalent to that which would have been present if 50% of the diet had consisted of cotton-seed flour. Similarly, the requisite amount of ether-soluble accessory substance is that which can be extracted from cotton-seed flour equivalent to 138% of the diet.

Experiments are also described in which cotton-seed flour constituted the sole source of protein in the diet, adequate supplies of other necessary ingredients being furnished by suitable materials. Under these conditions, normal growth of rats and their offspring is achieved when the diet contains not less than 18% of cotton-seed flour.

H. W. B.

Nutritive Value of the Diamino-acids occurring in Proteins for the Maintenance of Adult Mice. E. M. K. GRILING (*J. Biol. Chem.*, 1917, **31**, 173—199. Compare Ackroyd and Hopkins, this vol., i, 237; and Abderhalden, A., 1916, i, 580).—The removal of the diamino-acids from hydrolysed caseinogen by means of phosphotungstic acid renders it no longer adequate for the maintenance of adult mice when it constitutes the sole source of nitrogen in their diet. If, now, cystine and either arginine or histidine are added, the efficiency of the diet is restored. Apparently arginine and histidine may completely replace each other in a diet without affecting its efficiency, whilst the presence of lysine is unnecessary for the maintenance of mice.

The disappearance of the nutritive efficiency of caseinogen on heating for an hour in an autoclave at 7 kilos. pressure is confirmed (McCollum and Davis, A., 1916, i, 183).

H. W. B.

How are the Plant Proteins of the Diet Utilised in the Animal Body? II. H. BORUTTAU (*Biochem. Zeitsch.*, 1917, **82**, 96—102. Compare A., 1915, i, 616).—To dogs, after an interval of nitrogen-free diet, were administered diets containing known amounts of nitrogen of vegetable origin; a period of nitrogen-free feeding followed. The nitrogen excreted in urine and faeces during these periods was estimated, and from the results the biological value was calculated by the two formulæ of Thomas. The results seem to indicate that the physiological evaluation of the proteins is somewhat complex, as no very definite conclusions are to be drawn from the limited number of experiments described.

S. B. S.

Permeability of Cells. VII. Resorption of Proteins and their Degradation Products from the Peritoneal Cavity of the Rabbit. MARCUS KJÖLLERFELDT (*Biochem. Zeitsch.*, 1917, **82**, 188—225. Compare A., 1916, i, 450).—It was difficult to determine the resorption of casein, owing to the formation of exudates. Of peptone introduced into the peritoneal cavity, 15% was absorbed in thirty minutes and 24% in sixty minutes; 40% of hydrolysed casein was absorbed in sixty minutes; 50—65% of

a a*

amino-acids were absorbed in sixty minutes. There was an appreciable difference in the rate of absorption of the different amino-acids, but an insufficient number of experiments have been carried out to determine accurately their relative absorability.

S. B. S.

Proteoclastic Tissue Enzymes of the Spleen. MAX MORSE (*J. Biol. Chem.*, 1917, **31**, 303—306).—The proteins of the spleen are hydrolysed during autolysis by a proteoclastic enzyme which operates only in a neutral, or preferably slightly acid, medium, and corresponds with the β -protease described by Hedin (A., 1904, ii, 58). The other enzyme in the spleen, α -protease, exerts its action in an alkaline medium and hydrolyses peptone or fibrin, but is without action on the native proteins of the spleen. The latter enzyme is therefore not a true autolytic enzyme, and probably is derived from the leucocytes in the spleen instead of from true splenic tissue.

H. W. B.

Transformation of Arginine into Creatine in the Animal Organism. B. C. P. JANSEN (*Arch. Néerland. Physiol.*, **1**, 618—624. Compare Thompson, this vol., i, 369).—An increase in the tonus of a muscle is known to be attended by the production of creatine (Pekelharing and van Hoogenhuyze, A., 1910, ii, 324). It is now shown that increased tonus is accompanied by a disappearance of arginine which corresponds in amount with the creatine produced in the muscle. The author draws the conclusion that creatine is formed directly from arginine.

The amount of arginine in muscle is estimated after hydrolysis by treating equal parts of the neutralised hydrolysate with urease, and a mixture of urease and arginase respectively. After incubation, the amount of arginine is calculated from the difference in the amounts of ammonia obtained by distillation from the two portions.

H. W. B.

A New Olfactometer. C. VAN DAM (*Arch. Néerland. Physiol.*, 1917, **1**, 660—665).—The odoriferous material is mixed in any desired proportion with 10 grams of melted paraffin (m. p. 60°) and cast into cylinders 3.5 cm. long and 0.6 cm. in diameter. These are fixed into small copper tubes $1\frac{1}{2}$ cm. in length, which can be screwed on to a copper rod, 10 cm. in length.

The olfactometer is made of glass, and consists of an air tube, 1.5 cm. in diameter and 16 cm. long, into one end of which two tubes are fused, each 8 cm. long and 0.6 cm. diameter, at right angles to each other. One of these, the carrying tube, into which the odoriferous cylinder slides, has the same axis as the air-tube and penetrates it to a depth of 6 cm. The other, to the outer end of which the nose is applied, is perpendicular to the air and carrying tubes. The odoriferous cylinder, with its attachments, is placed in the carrying tube and gently pushed in until a smell is just perceived by the nose at the end of the perpendicular tube. The cylinder is then pushed just a little further until the odour is

distinctly recognised. The length of the wax cylinder which emerges from the internal aperture of the carrying tube is taken as a measure of the odoriferous power of the material experimented with.

Certain advantages relating to simplicity of apparatus and accuracy of results are claimed for this method as compared with that of Zwaardemaker.

H. W. B.

Adsorption of Odoriferous Substances. C. VAN DAM (*Arch. Néerland. Physiol.*, 1917, 1, 666—677).—The author investigates the relative power of different materials, such as gold, silver, platinum, iron, wood, ebonite, glass, quartz, bone, etc., to adsorb the odour of certain volatile liquids, ionone, eugenol, acetophenone, nitrobenzene, etc.

A drop of the odoriferous liquid is placed by means of a thin rod on the bottom of a cylindrical flask, which is then stoppered. When the odour has become uniformly distributed, a cylinder of the material the adsorptive capacity of which is to be measured is introduced into the flask and allowed to remain in contact with the vapour for one minute. It is then withdrawn, and the amount of odoriferous substance adsorbed is measured by means of the olfactometer previously described (compare preceding abstract). The procedure is then repeated with a cylinder of another material.

The results are variable, and, although there are indications of the dependence of the degree of adsorption of the odour of various substances on their chemical constitution, the author nevertheless draws the conclusion that definite quantitative relations cannot yet be established.

H. W. B.

Adsorption of Odoriferous and other Substances by Lipoids. J. H. KREMER (*Arch. Néerland. Physiol.*, 1917, 1, 715—725).—By means of a spectroscopic method, the author shows that when air saturated with an odoriferous substance, such as pyridine or camphor, is bubbled through a liquid containing a lipid, such as a suspension of lecithin or of fatty animal tissue in Ringer's solution, more odoriferous substance is adsorbed than when the saturated air passes through water. The bearing of these results on Overton's theory of narcotic action is discussed.

H. W. B.

Relation between Odour and Constitution. H. J. PRINS (*J. Soc. Chem. Ind.*, 1917, 36, 942—943; from *Perf. and Essent. oil Rec.*, 1917, 8, 222—223).—Majewski's theory (*A.*, 1902, i, 103) that the odour of substances is due to the presence of 'osmophoric' groups has been modified by Marchand (*Deuts. Parf. Z.*, 1915, 232, 243, 287), who concluded that the non-osmophoric part of the molecule determined the class of odour, whilst its shade or tinge depended on the osmophoric group. It is more correct to regard all groups as osmophoric, but different in strength. Thus the odour of derivatives of benzene is similar because the substituting groups cannot entirely overcome the osmophoric influence of the benzene

molecule. On the other hand, the different odours of octyl alcohol, octaldehyde, and octoic acid demonstrate the weak osmophoric influence of the aliphatic hydrocarbons. Chemically homologous substances have similar odours, for example, octaldehyde, nonaldehyde, and decaldehyde, and octyl, nonyl, and decyl alcohols. If an alteration in the hydrocarbon part of an aromatic substance has a great influence on the chemical character of the strongest osmophoric group, there will be a considerable change in the odour (compare the difference in odour between lauraldehyde and methyl-nonylacetaldehyde). Double bonds in the neighbourhood of an alcoholic, aldehydic, or carboxylic group have a marked influence on odour (compare decaldehyde with undecenaldehyde, citronellal with citral, α -ionone with β -ionone). Of two changes in the constitution of a compound, the odour will be most affected by that which has the strongest influence on the most powerful osmophoric group. The influence of formic acid preponderates over that of alcohols in the formic esters, the preponderance being least in the formates of strongly osmophoric alcohols, such as borneol and menthol. H. W.

Relation of the Quality of Proteins to Milk Production.

III. E. B. HART and G. C. HUMPHREY with BARNETT SURE (*J. Biol. Chem.*, 1917, **31**, 445—460. Compare Hart, Humphrey, and Schaal, A., 1916, i, 771).—Similar experiments to those already described have been carried out with a basal ration containing clover hay instead of corn stover. In these circumstances, positive nitrogen balances were maintained during most of the period of observation (sixteen weeks) with a slow shrinkage in milk volume, but a maintenance of the percentage composition of the milk. The replacement of the corn stover by clover hay therefore increases the efficiency of the protein concentrates added to the basal diet of cows, especially in the case of the gluten feed. H. W. B.

Distribution of the Fatty Acids in the Milk Fat of the Cow and Sheep. CHARLES CROWTHER and ALEXANDER HYND (*Biochem. J.*, 1917, **11**, 139—163).—The amounts of the different fatty acids present in milk or butter-fat are estimated by converting them into methyl esters and then subjecting the mixed esters to fractional distillation. The preparation of the methyl esters is accomplished by heating the fat in ethereal solution with excess of methyl alcohol containing a small proportion of hydrogen chloride. The mixed esters are separated from the neutralised reaction mixture and then fractionally distilled three or four times, in each case under atmospheric pressure until a temperature of 150—160° is reached, and subsequently under diminished pressure. A series of fractions is obtained, each of which contains only two saturated esters and one unsaturated ester, which is found to be methyl oleate in each case. From the iodine absorption and the saponification values of each fraction the weight of each ester contained in it is calculated. By summing up the results for the individual fractions, the weight of each acid in the original weight of fat taken is readily determined. A control using an artificial mixture of the

acids occurring in butter-fat was carried out with satisfactory results. On an average, it is found that the total loss of esters incurred during the whole estimation amounts to less than 1% of the weight of fat taken for analysis.

By the application of this method the fat contained in the "first runnings" of milk from a cow is shown to differ considerably from the fat contained in the "last runnings," or "strippings"; whilst the milk-fat of the cow shows distinct differences from that of the ewe. The average percentage amounts of fatty acids in normal butter-fat are as follows: Butyric, 4.27; hexoic, 1.64; octoic, 1.16; decaoic, 1.19; lauric, 5.01; myristic, 16.43; palmitic, 14.83; stearic, 3.40; dihydroxystearic, 0.38; and oleic, 44.42. H. W. B.

Blood Lipoids in Anæmia. W. R. BLOOR and D. J. MACPHERSON (*J. Biol. Chem.*, 1917, **31**, 79—95).—The authors have examined the distribution of the lipoids in the blood of numerous persons suffering from anæmia. As long as the percentage of corpuscles in the blood remains above half the normal value, the percentages of the various lipoids are the same as those associated with healthy blood. When the percentage of corpuscles falls below this limit, the plasma usually contains an excessive amount of fat, whilst there is a decrease in the amounts of cholesterol and lecithin. The corpuscles in nearly all cases have the normal content of lipoids, which indicates that the anæmic condition is not due to an abnormal susceptibility of the corpuscles to hæmolysis. The normal relation between the free and combined cholesterol in the blood plasma is also unaltered in anæmia, which lends no support to the view that anæmia is associated with an abnormally large combination of cholesterol as ester.

The low values for lecithin and the high values for fat which are generally most marked in those cases where the percentage of blood corpuscles is lowest are regarded by the author as due to deficient assimilation of fat in the blood, resulting from the lack of sufficient corpuscles to bring about the change of fat to lecithin, which is believed to be one function of the corpuscles (Bloor, A., 1916, i, 450). The authors direct attention to the low values for cholesterol, which is an antihæmolytic substance, and to the high fat fraction, which suggests the presence of abnormal amounts of hæmolytic substance in the blood in the anæmic condition.

Splenectomy, in anæmic, as in normal cases, is followed by a rise in the percentage of lecithin and fatty acids in the corpuscles and of cholesterol in the plasma. H. W. B.

Effect of Hydrochloric Acid on the Mineral Excretion of Dogs. RAYMOND L. STEHLE (*J. Biol. Chem.*, 1917, **31**, 461—470).—The administration of hydrochloric acid to dogs causes an increased excretion of calcium and magnesium, as well as of sodium and potassium, in the urine and fæces. After two or three days a retention of sodium and potassium occurs, which compensates for the preliminary loss observed. By far the larger proportion of the ingested acid is eliminated in combination with ammonia. H. W. B.

Diverse Physiological Behaviour of certain Stereoisomeric Alcohols of the Cholesterol Series. A. WINDAUS (*Nachr. K. Ges. Wiss. Göttingen*, 1916, 301—304; from *Chem. Zentr.*, 1917, i, 1017—1018).—It is well known that stereoisomerides may differ in their physiological behaviour, but the chemical processes which are caused by such differences do not appear to have been definitely investigated. Certain alcohols of the cholesterol series, notably β - and ϵ -cholestanol, are specially adapted for an examination of this question. Experiments have shown that β -cholestanol, like cholesterol, inhibits the hæmolytic action of certain blood poisons, for example, the saponins (digitonin), possessing in this respect approximately the same activity as cholesterol itself. ϵ -Cholestanol, on the other hand, is far less active than the β -compound, and only shows slight anti-hæmolytic action towards saponins. Experiments were performed with the following solutions: (a) fresh de-fibrinated ox-blood (5 c.c.) diluted with physiological salt solution to 100 c.c.; (b) solution of digitonin (1 part) in water (10,000 parts); 1 c.c. of this solution hæmolyzes 5 c.c. of diluted ox-blood; (c) solution of cholesterol or β - or ϵ -cholestanol (1 part) in methyl alcohol (200 c.c.). In every case precautions were taken to have the solution containing 0.9% of sodium chloride. The experiments lasted for twenty-four hours, the temperature being 18—20°. Five c.c. of diluted blood showed no hæmolysis with digitonin solution (1.5 c.c.), cholesterol solution (1.5 c.c.), and salt solution (2 c.c.) or with digitonin solution (2 c.c.), cholesterol solution (2 c.c.), and salt solution (1 c.c.). β -Cholestanol showed similar behaviour, whilst, in presence of ϵ -cholestanol complete hæmolysis occurred. The use of a large excess of the latter compound gradually weakens the action of digitonin, probably owing to absorption. According to Windaus (A., 1909, i, 920), the anti-poisonous action of cholesterol towards saponins depends on the formation of an additive compound of cholesterol and digitonin, which is almost inactive physiologically. β -Cholestanol likewise yields additive compounds with digitonin and other saponins, differing thus from the ϵ -compound (A., 1916, i, 813). The differing physiological behaviour of the stereoisomeric cholesterol alcohols is therefore to be attributed to their ability or inability to form inactive complex compounds.

H. W.

Fate of Inositol Administered to Dogs. ISIDOR GREENWALD and MORRIS L. WEISS (*J. Biol. Chem.*, 1917, 31, 1—14. Compare R. J. Anderson, A., 1916, i, 688).—Subcutaneous injection of inositol into normal and phloridzinised dogs in a fasting condition is accompanied by a slight increase in the value of the urinary D/N ratio. Only small amounts of unchanged inositol appear in the urine. Corresponding with the increased excretion of dextrose, there is a slight decrease in the elimination of acetone and β -hydroxybutyric acid. It appears, therefore, that inositol is slowly converted into dextrose in the animal organism.

H. W. B.

Physiological Behaviour of Raffinose. SHIGENOBU KURIYAMA and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1917, **31**, 125—147).—Raffinose is devoid of nutritional value until after it has been hydrolysed. After parenteral injection into rabbits in doses of from 2 to 3 grams per kilo. of body-weight, 88% of the injected raffinose is recovered unchanged in the urine. When it is introduced directly into a loop of the small intestine of a dog it is unchanged, and can be recovered almost quantitatively after two hours. Human saliva, the bile, pancreas, liver, and mucous membranes of the small and large intestines of the dog and rabbit do not contain raffinase; the gastric juice exerts a slight hydrolytic action under certain conditions on raffinose.

When raffinose is fed to animals, it is hydrolysed in the large intestine by bacteria. The same effect is observed when the raffinose is introduced directly into the large intestine, and the resulting compounds are utilised in the body. It is probable that bacteria capable of hydrolysing raffinose occur most frequently in the large intestines of species of animals which consume foods containing raffinose.

Raffinase (from yeast) exerts its maximum activity in a medium of which the hydrogen-ion concentration (pH) lies between 3·8 and 5·4.

H. W. B.

The Toxicological and Urological Characterisation of 2:4-Dinitrophenol. L. LUTZ and G. BAUME (*J. Pharm. Chim.*, 1917, [vii], **16**, 61—62).—2:4-Dinitrophenol, of which the toxicity coefficient is above 0·2 gram per kilo. of body-weight of the animal, passes through the animal unchanged, and is found in the urine. For its detection, the organic matter is destroyed by sulphuric acid, and the solution boiled to eliminate formaldehyde. The dinitrophenol is extracted by light petroleum, the solvent is evaporated, and the residue dissolved in water. The presence of dinitrophenol is shown by the formation of a red or pale pink coloration when this solution is boiled with a freshly prepared solution of potassium cyanide, or by the formation of an orange-red ring when a solution of ammonium sulphide is added to the aqueous solution of the dinitrophenol, which has been mixed with its own volume of aqueous sodium hydroxide.

W. G.

Intravenous Injections of β -Hydroxybutyric and Acetoacetic Acids. RUSSELL M. WILDER (*J. Biol. Chem.*, 1917, **31**, 59—65).—The intravenous injection of levorotatory sodium β -hydroxybutyrate into dogs does not lead to the appearance of β -hydroxybutyric acid in the urine until the rate of injection reaches 0·4 gram per kilo. of body-weight per hour. Sodium acetoacetate appears in the urine when the rate of its injection into the blood is 0·2 gram per kilo. of body-weight per hour. When the rate of injection of sodium acetoacetate is increased to 0·4 gram per kilo. of body-weight per hour, β -hydroxybutyric acid is eliminated in the urine. The author draws the conclusion that, under the conditions of the experiment, the acetoacetic acid is

converted almost quantitatively into β -hydroxybutyric acid. No evidence of the reverse change was obtained. H. W. B.

Pharmacological Studies of the Ipecacuanha Alkaloids and some Synthetic Derivatives of Cephaeline. I. Toxicity. A. L. WALTERS and E. W. KOCH (*J. Pharm. Expt. Ther.*, 1917, 10, 73—81. Compare Karrer, A., 1916, i, 833, and Meader, A., 1916, i, 834).—The authors have measured the relative toxicity of the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, amyl, isoamyl, and allyl ethers of cephaeline. The substitution of the methyl group in emetine (cephaeline methyl ether) by radicles of the higher homologous alcohols markedly decreases the toxicity for rats, guinea-pigs, and rabbits. The isoamyl ether is the least toxic of the series, having about one-fifth the toxicity of emetine when given subcutaneously.

Emetine is not a very toxic alkaloid when given in a single dose, but is dangerous when given repeatedly in small doses over a considerable period of time. H. W. B.

Alleged Antineuritic Properties of 2-Hydroxypyridine and Adenine. ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1917, 11, 172—179. Compare Williams, A., 1916, i, 697, and this vol., i, 353).—The authors confirm the existence of 2-hydroxypyridine in two crystalline forms, but fail to observe any curative action of either form on polyneuritic pigeons. Similar negative results are recorded for adenine (compare Williams, *loc. cit.*).

H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Vital Stains. WERNER SCHULEMANN (*Ber.*, 1917, 50, 772—774; see also this vol., i, 369).—Polemical in reply to Skraup (this vol., i, 369; A., 1916, i, 869). D. F. T.

Bacillus paralacticus. F. DUCHÁČEK (*Biochem. Zeitsch.*, 1917, 82, 31—47).—*B. paralacticus* was isolated from lactobacilline. It produces in milk 0.6—0.7% lactic acid, whereas *B. bulgaricus* produces under the same conditions 2.3—2.5%. The whole amount of the fermented sugar in the milk is converted into lactic acid. If the bacillus acts in the presence of the neutralised medium (in the presence of calcium carbonate), 50% of the sugar can be fermented in four months. Under the same conditions, *B. bulgaricus* can cause fermentation of the whole of the sugar within ten to fourteen days. The reason of this difference is that the coagulum produced in the fermentation is sufficiently acid to inhibit the action of the former species of bacillus. The best

medium for the growth of *B. paralacticus* is peptonised malt extract containing a suitable sugar. A further distinction between *B. bulgaricus* and *B. paralacticus* is that the latter produces *r*-lactic acid, whereas the former produces an inactive acid. About 4·6% of the acid produced is in both cases acetic acid. S. B. S.

Colour Changes Produced by Two Groups of Bacteria on Caseinogen and certain Amino-acids. ELFRIDA CONSTANCE VICTORIA CORNISH and ROBERT STENHOUSE WILLIAMS (*Biochem. J.*, 1917, 11, 180—187).—Discoloured Stilton cheese contains a very large number of micro-organisms belonging to many different groups. Similar micro-organisms are present in the milk from which the cheese is made, and also in the water supplies of the farms from which the milk is obtained. The authors have arbitrarily selected certain members of two of these groups, and have studied their action on caseinogen and amino-acids from the point of view of colour production.

The two groups selected were the *B. proteus* group and a group of bacilli which were Gram-negative and produced an alkaline reaction in solutions of various sugars, alcohols, etc., into which they were inoculated. The results show that the members of the former group produced a well-marked amber colour in media containing tryptophan, whilst those of the latter group caused a yellow colour to appear in media containing tryptophan and a definite brown colour in caseinogen solutions. H. W. B.

The Extraction of Different Preparations of Dried Yeast. EDUARD BUCHNER and SIEGFRIED SKRAUP (*Biochem. Zeitsch.*, 1917, 82, 107—133).—From acetone-treated yeast, the zymase, protein, and endotryptase can only be extracted by water after grinding. This is not the case, however, with air-dried yeast prepared by Lebedev's process. From such preparations, the zymase, etc., are readily extracted by water, and previous grinding does not improve the extracts. The authors discuss in some detail the structure of the yeast and the theories put forward to explain the relationships between the ferments and the protoplasm. S. B. S.

The Action of Toluene on Fermentation Processes. EDUARD BUCHNER and SIEGFRIED SKRAUP (*Biochem. Zeitsch.*, 1917, 82, 134—140).—Toluene has practically no influence on the rate of fermentation by acetone preparations of yeast. This is not in accordance with the results of Euler and Kullberg. On repeating their experiments (at 31°) with Lebedev preparations or maceration juice made therefrom, it was found that toluene did inhibit fermentation, as these authors observed. The inhibition took place, however, only in the earlier stages of the fermentation; in later stages this could not be observed; in fact, after the first inhibition, the rate increased somewhat in the presence of toluene. S. B. S.

Influence of Available Carbohydrates on Ammonia Accumulation by Micro-organisms. SELMAN A. WAKSMAN (*J. Amer. Chem. Soc.*, 1917, 39, 1503—1512).—The growth of

Aspergillus niger and *Citromyces glaber* in a peptone medium, with and without added sucrose, has been studied. It is found that, in the absence of sugar, the organisms grow slowly, but that ammonia accumulates rapidly, whereas in the presence of sugar, the weight of mycelium increases rapidly until auto-digestion sets in, the amount of ammonia produced is very small as long as sufficient carbohydrate remains, but the peptone disappears rapidly. In the absence of sugar, therefore, the fungus attacks the protein for its fuel and carbon requirements, and so sets free an excess of nitrogen as waste ammonia. If sugar is added, the protein is almost entirely used in producing fungus mycelium, no waste ammonia being left over, and the carbohydrate is drawn on for fuel.

The results have an obvious bearing on some soil problems, particularly the ill-effects of adding available carbohydrates to the soil. The soil bacteria and fungi make a preferential attack on the carbohydrate and release very little surplus nitrogen as ammonia from the proteins. However, the judicious application of small quantities of a carbohydrate to the soil might be advantageous in stimulating the early development of more micro-organisms.

J. C. W.

Citric Acid Fermentation of *Aspergillus niger*. JAMES N. CURRIE (*J. Biol. Chem.*, 1917, **31**, 15—37).—According to the author, the fermentation of a sugar by *Aspergillus niger* may be regarded as an oxidation proceeding in three stages, producing citric acid, oxalic acid, and carbon dioxide respectively. He has attempted, therefore, to ascertain the best conditions for accelerating the first and depressing the last two stages in the process. By a judicious selection of cultures and conditions, the production of citric acid can be varied from none at all to more than 50% of the sugar consumed.

The conditions especially favourable for the production of citric acid are a high concentration of sugar and a low concentration of nitrogen, the nitrogen being supplied as ammonium salts rather than as nitrates. When nitrogen is supplied in the form of ammonium salts or as asparagine, iron does not stimulate the metabolic processes in any way, but when the supply of nitrogen is in the form of nitrates, iron has a marked stimulating effect, especially noticeable in the increased production of carbon dioxide.

The addition of calcium carbonate to reduce the growing acidity of the culture medium is deprecated; indeed, the fermentation is found to proceed best in a fairly acid medium. The most suitable medium for conducting the citric acid fermentation by *Aspergillus niger* contains 12.5% to 15% of sucrose, 0.2% to 0.25% of ammonium nitrate, 0.075% to 0.1% of potassium dihydrogen phosphate, 0.02% to 0.025% of crystallised magnesium sulphate, and 0.4 to 0.5 c.c. of *N*/5-hydrochloric acid, corresponding with a *pH* of 3.5 to 3.4. The addition of the acid greatly reduces the dangers of infection with organisms which might interfere with the citric acid fermentation. Under the prescribed conditions, the amount

of citric acid produced reaches its maximum about the eighth day, and the medium then contains about 10% of citric acid.

Variability in the fermenting power of cultures which cannot be distinguished on morphological grounds is often observed, and good results can only be obtained by careful selection of the moulds to be employed. When the fermentation proceeds properly, the mould does not form spores, but remains quite white. H. W. B.

The Action of Soaps on the Fermentative Degradation of Starch and Glycogen. SIEGMUND KENDE (*Biochem. Zeitsch.*, 1917, 82, 9—30).—The soaps of the higher fatty acids inhibit the degradation by diastase of starch and glycogen. This action differs from the ordinary action of ferment inhibitors in that the soap does not act directly on the enzyme, but on the substrate, with which it forms what is apparently an adsorption compound. Soaps will not inhibit, for example, the degradation of dextrans by diastase. The inhibitory action is annihilated by the presence of small quantities of acids. The results were obtained by the author as a result of investigations of the inhibitory action of the expressed juice of pancreas on the action of diastase, which he succeeded in proving to be due to the presence of soaps contained in such juice. He discusses in some detail the physiological function of the soaps, especially in the relationship to the glycogen fixation in the liver. S. B. S.

Nitrate Assimilation. O. LOEW (*Ber.*, 1917, 50, 909—910).—A reply to Baudisch (this vol., i, 434). A reaffirmation that nitrate assimilation is not a photochemical process (see A., 1912, ii, 797).

J. C. W.

The Development of the Typical Glucosides of the Leaf in Germinating and Growing Digitalis Plants. WALTHER STRAUB (*Biochem. Zeitsch.*, 1917, 82, 48—59).—The amount of the glucosides in different stages of the growth of the plant was estimated by a pharmacological method (by ascertaining the number of lethal doses for a frog in different fractions). The glucosides in question are digitalinum verum and digitalein, which are soluble in water, and both of which are found in the seeds, and digitoxin, which is insoluble in water, but soluble in chloroform, and "gitalin," which is soluble in chloroform and cold water, which are found in the leaves. Digitalein also occurs in the leaves. As a result of pharmacological tests of the fractions obtained from plants in various stages of the growth, a very approximate quantitative estimation of these alkaloids could be made. It was found that the glucosides of the seeds are not reserve material, but disappear during germination, and are stored in the leaves, in which organs they do not increase further in quantity. The glucosides proper of the leaves make their first appearance in the earliest foliage leaves and continue to increase in quantity until they form 1% of the dried matter. Reasons are given for sup-

posing that they are only waste products of the metabolism of plant growth. S. B. S.

Function of Calcium in the Nutrition of Garden Pea Seedlings with Ammonium Salts. V. A. MORSOV (*Papers from Lab. of Prof. Prianichnikov, Moscow Institute of Agriculture*, 1916, **10**, 391—395; *Bull. Agric. Intell.*, 1917, **8**, 214—216; from *J. Soc. Chem. Ind.*, 1917, **36**, 898).—In the assimilation of ammonium salts by plants, the base is absorbed and the acid left; this acid requires to be neutralised if continued assimilation is to go on. Experiments were made with sprouted seeds of the garden pea grown in solutions of ammonium sulphate alone, ammonium sulphate and calcium carbonate, and ammonium sulphate and ferric hydroxide. The best development of the seedlings occurred with the solution containing calcium carbonate, the second best with ferric hydroxide, whilst that with ammonium sulphate alone was poorer than with distilled water. The greatest accumulation of total nitrogen and asparagine nitrogen in the seedling also occurred with calcium carbonate followed by ferric hydroxide, whilst the ammoniacal nitrogen was least with calcium carbonate. Thus calcium carbonate does not act merely as a neutralising agent, but the calcium present also exerts its own specific nutritive influence. T. S. P.

Rôle of Ammonia in the Metabolism of Nitrogenous Substances in Plants. D. N. PRIANICHNIKOV (*Collected Papers of Agronom. Inst. of Moscow*, 1916, **10**, 1—24; *Bull. Agric. Intell.*, 1917, **8**, 204—211; from *J. Soc. Chem. Ind.*, 1917, **36**, 898).—In the life of the higher plants, ammonia plays an important part as the starting point for the synthesis of protein and as an end-product in the oxidation of nitrogenous substances. It does not, however, accumulate as such, but is converted into asparagine.

Plants may be divided into three types, according to the facility with which they accomplish this synthesis of asparagine: (a) Plants which readily absorb ammonia from solution and convert it into asparagine. *Hordeum sativum* (barley), *Zea mais* (maize), and *Cucurbita pepo* (pumpkin) belong to this group. (b) Plants in which the absorption of ammonia is very feeble, and the presence of ammonia in the culture solution retards the oxidation of nitrogenous substances. The absorption of ammonia can be increased by adding calcium carbonate to the culture solution. *Pisum sativum* (pea) and *Vicia sativa* (vetch) are plants of this type. (c) Plants in which the presence of ammonia in the culture solution prevents the conversion of ammonia into asparagine. The addition of calcium carbonate has no effect in these cases. The yellow lupin (*Lupinus luteus*) is an example of this type.

T. S. P.

Various Modes of Combination of Methyl Alcohol in Plants. Estimation of Pectin- and Lignin-Methyl Alcohol in Roots. TH. VON FELLEBERG (*Mitt. Lebensmittelunters. Hyg.*, **8**, 1—29; from *Chem. Zentr.*, 1917, **i**, 1154—1155).—In addition to

pectin, the majority of plants contain other methoxy-compounds in which the methoxy-group is more firmly combined and is not eliminated by sodium hydroxide. In such cases, methyl ethers are obviously present. Since Zeisel's process is somewhat cumbersome and does not allow a distinction between the methyl groups present in ester or ether groups, the author has modified his previous process (A., 1916, ii, 351). This also presents the advantage of only indicating methyl groups, whilst, by Zeisel's methods, other alkyl groups are also eliminated. The lignocelluloses, and also suberin, contain firmly-bound methyl alcohol.

The literature of the lignocelluloses is reviewed, and the analyses recorded therein lead the author to propose the formula $C_{22}H_{19}O_9Me_2$ for the hypothetical lignin of wood. In accord with König and Rump, the author includes under the term 'lignin' those non-volatile, methoxy-compounds of plants which are insoluble in alcohol and ether and do not yield methyl alcohol when treated with sodium hydroxide, but do so with concentrated sulphuric acid. Since the methoxy-content of these substances is variable and generally unknown, and the compounds can only be recognised by their methoxy-content, the author prefers to consider them as 'lignin-methyl alcohol,' and not as 'lignin.' The assumption of König and Rump (*Zeitsch. Nahr. Genussm.*, 18, 177), that cellulose and lignin are only intimately associated and not chemically united in the crude fibres, is not justified by the evidence they adduce.

In connexion with the form of occurrence of methyl alcohol in plants, the author has examined pine wood, cork, normal and brown hay, roots and their adulterants, cocoa and cocoa shells. It is found that the pectin of wood is not identical with that of fruit, since it is insoluble in water and not dissolved when heated under pressure with organic acids. Cork contains several methoxylated acids and a certain proportion of lignin, the methyl alcohol of which constitutes about 25% of the total methyl alcohol. In the fermentation of brown hay, methyl alcohol is eliminated from the pectin and partly oxidised to formic acid; simultaneously, an increase occurs in the lignin-methyl alcohol.

For the estimation of total methyl alcohol, the finely ground sample, freed from fat if necessary (0.2—0.5 gram), is heated to gentle ebullition for ten minutes with sulphuric acid (72%, 15 c.c.). After cooling, water (25 c.c.) is added, and the mixture is distilled until 25 c.c. have been collected. The distillate is made alkaline with sodium hydroxide, and again distilled until 16.2 c.c. have passed over. With substances of low methoxyl content, two further distillations are performed, in which 10 c.c. and 6 c.c. respectively are collected. The final distillate is weighed and colorimetrically investigated, as previously described. The lignin-methyl alcohol is deduced from the differences between the values for the total and pectin-methyl alcohol. When very small quantities of lignin are present, it is advisable to estimate both forms in the same sample; the distillation residue obtained after estimation of the pectin is filtered, washed with hot water, alcohol, and ether, dried, and distilled with sulphuric acid.

H. W.

The Biochemical Phenomena of Oxido-reduction. JACQUES EMIL ABELOUS and JULES ALOY (*Compt. rend.*, 1917, **165**, 270—272).—The authors have repeated Bach's work (compare this vol., i, 375) on the reducing enzyme present in milk and potatoes, and find that a large number of substances, in addition to aldehydes, act as co-enzymes. Such substances are amines, compounds with heterocyclic rings such as quinoline, terpenes, and even inorganic compounds such as manganous salts. The presence of a substance readily oxidised is sufficient for the reduction of nitrates or chlorates to occur when added to fresh milk. In the case of the precipitate obtained from potato juice on the addition of alcohol, the reducing action of its enzyme is apparently favoured by the presence of starch and amylase. W. G.

The Carbohydrates of Lichens. B. TOLLENS (*J. pr. Chem.*, 1917, [ii], **95**, 132).—Attention is directed to a paper by Ulander and Tollens (*A.*, 1906, ii, 193) on this subject. D. F. T.

Analysis of Ragweed Pollen. FREDERICK W. HEYL (*J. Amer. Chem. Soc.*, 1917, **39**, 1470—1476).—An analysis of the pollen of ragweed (*Ambrosia artemisiifolia*) has been undertaken, as it is regarded in America as the chief cause of "hay fever" or autumnal catarrh. The grain is spherical, of an average volume of $9 \cdot 7$ cubic mm., and the cell-wall constitutes about 65% of the whole. The following composition was determined: moisture, 5·3%; crude fibre, 12·2%; pentosans, 7·3%; ash, 5·4%; dextrin, 2·1%; protein, 24·4%; soluble in alcohol, 42·9%, consisting of fat, 10·8%, lecithin, 0·75%, sucrose, 0·4%, dextrose, 1·6%, resin, 17·4%, and a nitrogenous base. Of the protein, about 7·5% could not be extracted, 6·75% was soluble in alkali, and about 5% could be extracted by 10% salt solution. Ragweed pollen contains much less protein, especially albumin and globulin, than rye pollen. Two hay fever subjects were found to show characteristic ophthalmic disturbances with amounts of the protein of the order of $1 \cdot 6$ to $5 \cdot 6$ grams, that is, about the same as the minimum amount of rye pollen protein. J. C. W.

Action of Coal Gas on Plants. III. Action of Coal Gas, whilst passing through Soil or Water, on Roots and Leafy Branches. C. WEHMER (*Ber. Deut. bot. Ges.*, 1917, **35**, 403—410. Compare this vol., i, 531).—In the present series of experiments, young annuals, such as cress, grasses, or beans, were grown in culture solutions through which coal gas was slowly bubbled, or in pots so arranged that gas could be led into the soil from above or below. In addition, leafy shoots of the lime, elder, privet, ilex, *Philadelphus*, and various conifers were kept under observation in culture solutions treated with gas.

It appears that undiluted coal gas is highly toxic for the roots of plants, but that the constituents which dissolve in water are not so acutely dangerous. The effect on young cress, for example, is much more striking if the gas is led up through the soil than it is if the gas is just led into the top layers.

The experiments on leafy shoots show that the ill-effects of coal gas on the upper parts of a plant are not always conditioned by damage to the roots, as some have supposed. Still, the effects of the ascent of water charged with the gas into the shoots vary remarkably from part to part of the shoot and from plant to plant. With the exception of the yew, most conifers are highly resistant, but the usual effect is an early shedding of the leaves, the rind and buds remaining practically unhurt. The unfolding of the buds on horse chestnut shoots is quite undisturbed in water charged with gas.

It is just as difficult to say which of the water-soluble constituents of coal gas is particularly toxic, that is, in the concentration in which it occurs in the gas, as it was in the earlier cases of the undiluted gas itself. In this connexion it is now reported that an atmosphere containing 1% of hydrogen sulphide is fatal to the seed or seedlings of cress, but that in the concentration 0.03%, that is, more than is commonly found in coal gas, this "poison" is distinctly beneficial to the germination of cress. J. C. W.

Sensitiveness of Plants to Poisoning with Coal Gas.

SARAH L. DOUBT (*Pharm. J.*, 1917, 99, 111; from *Bot. Gaz.*, 1917, 63, 209—224).—The increasing loss of plants in greenhouses and of trees in the streets of American towns is attributed largely to coal gas poisoning. On account of their sensitiveness in this respect, tomato plants, *Salvia splendens*, *Mimosa pudica*, *Ricinus communis*, *Datura stramonium*, and *Dianthus caryophyllatus* are suitable as test plants. With all these except the carnation, the presence of 50 parts of coal gas per million of air causes epinastic growth of petioles; the flower buds of carnations wither in this degree of pollution. A mixture of coal gas and air in the proportion of 1:1000 causes the leaves of the above plants to fall off, as well as those of *Coleus* and of *Hibiscus rosa sinensis*. Ethylene exerts a similar effect. The following plants are stated to be unaffected by a concentration not exceeding 1:400 of coal gas in air, which is the lowest concentration that can be detected by smell: *Calladium esculentum*, *Lupinus perennis*, *Eriobotrya japonica*, *Phoenix canariensis*, *Conocephalus* sp., *Canna*, *Achyranthes lindini*, *Alternanthera* sp., *Cytisus canariensis*, and species of *Polypodium*. Many trees, including elder, ash, lime, and catalpa, are very sensitive to gas escaping into the soil. The above-named gas-sensitive plants may be employed for the detection of slight contamination of the air by coal gas. H. B. H.

The Effect of Hydrogen and Hydroxyl-ion Concentration on the Growth of Barley Seedlings. D. R. HOAGLAND (*Soil Sci.*, 1917, 3, 547—560).—Barley seedlings were grown in partial nutrient solutions, having the same osmotic pressure but a considerable range of hydrogen- and hydroxyl-ion concentrations, this being obtained by the use of suitable mixtures of the three potassium phosphates. The hydrogen-ion concentrations were determined by hydrogen electrode measurements (compare Clark and Lubs,

A., 1916, ii, 513). The hydroxyl ion in such solutions was more toxic than the hydrogen ion for similar divergences from the neutral point. Solutions having a concentration of hydroxyl ion greater than 1.8×10^{-6} were distinctly injurious, and greater than 2.5×10^{-5} were very toxic. A concentration of hydrogen ion of approximately 0.7×10^{-5} was favourable to growth and produced no injury, but a concentration of 0.3×10^{-3} was very toxic. Microscopic examination showed injury to the root tips, and in many cases the leaves also gave evidence of toxicity. There was found to be a change in the hydrogen-ion concentration of the culture solutions after one or more days' growth. In general, the alkaline solutions decreased markedly in hydroxyl-ion concentration, acid solutions decreased slightly in hydrogen-ion concentration, and neutral solutions remained practically constant. W. G.

Does the Addition of Sulphuric Acid to the Soil Affect the Growth of the Beet? K. ANDRLÍK (*Zeitsch. Zuckerind. Böhm.*, 1917, 41, 685—688).—Instead of adding soluble nutrients to the soil, the author has thought it to be worth while to try the effect of applying cheap chemicals, like the mineral acids, to render more of the natural constituents of the soil available to the plant. He has compared the growth of sugar beet on field plots sprinkled before seed-time with dilute sulphuric acid (2—4 kilos. per acre) and on untreated plots, and finds indications that the weights of root and leaves are less, but the quantity and quality of the sugar slightly greater on the treated soil. J. C. W.

The White Turbidity of Wines. W. T. BARAGIOLA (*Zeitsch. Nähr. Genussm.*, 1917, 33, 513—520. Compare this vol., i, 373, 374).—The white turbidity which sometimes forms in wines is due to precipitation of ferric phosphate. The remedy is to oxidise the ferrous compounds by aeration and then to clarify the wine with gelatin. Sulphurous acid may be added to prevent further oxidation of ferrous compounds, but the addition of this acid is useless when the turbidity has once formed. W. P. S.

Distribution of Nitrogen in Beer. JOHN SMITH SHARPE (*Biochem. J.*, 1917, 11, 101—111).—The author has estimated the proportion of total nitrogen in light and strong beers, ales, and porter, combined as protein, amino-acid, and purine respectively. The results show that the protein nitrogen constitutes from 13.2% to 37% of the total nitrogen, which indicates that the amount of protein in beers varies from 0.038 to 0.185%. The amino-acid nitrogen varies from 25% to 46%, and the purine nitrogen from 25.8% to 52.4% of the total nitrogen, the former being present in beer to the amount of from 0.014% to 0.040%, and the latter from 0.010% to 0.039%. A small proportion of the nitrogen is combined in the form of an alkaloid resembling coniine (Chapman, T., 1914, 105, 1895) and a still smaller amount as a basic substance, which may be betaine. The total nitrogen in the beers analysed varied from 0.039% to 0.113%. H. W. B.

The Soil and Soil-solution. OTTO NOLTE (*J. Landw.*, 1917, 65, 1—66).—The author develops theoretical considerations concerning the soil and the liquid present in it on the basis of the law of mass action, and it is shown that an important part is played by the displacement of the chemical equilibrium in the soil as a result of the influence of the climate and of the actions of plants, animals, etc. T. H. P.

Action of Frost on the Soil. OTTO NOLTE and ERNA HAHN (*J. Landw.*, 1917, 65, 75—81).—Frost opens the texture of the soil in consequence of the expansion of the water present, and also, since it removes solvent in a solid state from the system, causes displacement of the equilibrium, the salts undergoing concentration or even precipitation. This action affects first those substances occurring in colloidal solution or in suspension. That such loosening effects soon vanish when the ground thaws, owing to the interstitial spaces becoming filled with water and particles of soil, is shown by successive freezing and thawing of an aqueous suspension of ultramarine particles of uniform size; each freezing increases the extent to which the particles become aggregated. T. H. P.

Soil Colloids. II. Influence of Colloids on Electrical Conductivity of Salts. M. I. WOLKOFF (*Soil Sci.*, 1917, 3, 423—430. Compare A., 1916, i, 784).—The inorganic colloidal particles, as found in clay, particularly the colloidal gels, reduce the electrical conductivity of solutions of salts, the interference being due possibly either to the fact that the colloidal particles, moving comparatively slowly, interfere with the passage of the free ions, or to the change of the structure of the gel at the point of coagulation, resulting in an increase in the adsorptive capacity of colloids. The adsorption of electrolytes by the gel increases with the increase of the electrolyte present for coagulation. The separation of colloids from crystalloids can be carried out by coagulation with certain electrolytes provided that only a minimum amount of electrolyte is used for complete coagulation. W. G.

The Action of Solutions of Ammonium Sulphate on Muscovite. R. F. GARDINER and EDMUND C. SHOREY (*J. Ind. Eng. Chem.*, 1917, 9, 589—590).—A statement of the results of preliminary tests showing that mica powder, generally considered one of the most stable of soil minerals, is attacked to a notable extent by dilute aqueous ammonium sulphate, approximately 20% of the potassium present being removed by contact with a 0.5—1% solution for twenty-four hours at 20°. D. F. T.

The Effect of Ammonium Sulphate on Soil Acidity. F. E. ALLISON and R. C. COOK (*Soil Sci.*, 1917, 3, 507—512).—Pot experiments have been carried out with different soils, varying in texture from a sand to a clay, to test the effect of the repeated application of ammonium sulphate to the soil on the soil acidity. In one series of experiments the soil was left fallow and in the other a crop of buckwheat was taken every three months.

Having regard to the fact that these were only single pot trials, the results show that, where no nitrogenous fertiliser was applied, the increase in acidity of each of the five soils during the year was practically the same, whether the soil carried a crop or was kept fallow. The presence of ammonium sulphate caused an increase in acidity considerably higher than in the control pots. On the average, the increase in acidity in these soils corresponded with about 3.6 kilos. of calcium oxide for every 4.5 kilos. of ammonium sulphate applied.

W. G.

Adsorption of Ammonium Sulphate by Soils and Quartz Sand. M. I. WOLKOFF (*Soil Sci.*, 1917, 3, 561—564).—A brief outline of work to be published in greater detail elsewhere. In the case of soils, the results show that, in general, with increase in concentration of the ammonium sulphate solution the percentage adsorption decreases, whilst the total amount of salt going out of solution increases. Quartz sand does not, however, entirely follow this general rule. On addition to the sand, the concentration of the salt solution apparently becomes greater. This is most pronounced in coarse sand, and diminishes as the fineness of the sand increases. The effect is more noticeable the more concentrated is the salt solution used, and when the dilution reaches a certain point for a given sand, then it follows the general rule given for soils.

W. G.

Effect of Different Salts on the Formation of Ammonia in Soil. GEORGE P. KOCH (*J. Biol. Chem.*, 1917, 31, 411—413).—The presence of small amounts of calcium dihydrogen phosphate increases the production of ammonia from dried blood in soil, whilst magnesium and potassium sulphates, singly or in combination, inhibit it. The toxicity of the magnesium and potassium salts is readily removed by the addition of a sufficient proportion of the calcium salt.

H. W. B.

Isolation of Cyanuric Acid from Soil. LOUIS E. WISE and E. H. WALTERS (*J. Agric. Research*, 1917, 10, 85—91).—Cyanuric acid has been isolated from an Indiana soil by extraction with dilute sodium hydroxide, acidification of the extract, and successive precipitation of the cyanuric acid as its mercury and lead salts. It was distinguished from tetracarbonimide by molecular weight determination and by analysis of its double silver-ammonium derivative. It was found to be present to the extent of 6.5 parts per million. The authors now find that the tetracarbonimide stated previously (compare A., 1915, i, 1092) to have been isolated from a loam soil was really cyanuric acid.

W. G.

Soil Constituents which Inhibit the Action of Plant Toxins. E. TRUOG and J. SYKORA (*Soil Sci.*, 1917, 3, 333—352).—In order to determine whether the inhibitive effect of certain soils to plant toxins was due to chemical or to physical factors, a series of pot cultures was carried out in which the physical character of the culture medium was controlled by using either

pure quartz sand or sand mixed with quartz flour or kaolin, whilst its chemical character was varied by the presence or absence of calcium carbonate. All pots received nutrient salts, and in addition the toxic substance under investigation. The test plants were wheat seedlings in all cases.

When copper sulphate was employed as the toxic agent, the increased soil surface obtained by the use of quartz flour and kaolin seemed to have a slight beneficial effect, but this was very small as compared with the effect of calcium carbonate, which completely neutralised any deleterious action of either copper sulphate or copper nitrate. With sodium arsenate, the wheat plants did better when the sand was mixed with quartz flour, but as this effect did not extend to the kaolin pots, it appeared probable that the improved growth was not due to the physical character of the quartz flour, but to certain impurities which it contained and which acted as catalytic agents in the oxidation of sodium arsenate; calcium carbonate was practically ineffectual. With guanidine carbonate, the presence of kaolin had a markedly beneficial effect on growth, but quartz flour had none, and the addition of calcium carbonate was actually deleterious. Assuming that kaolin may be regarded as an acid, the author points out that its probable action is to combine with the guanidine, thereby rendering the latter inactive. This hypothesis, which would also explain the ill-effects of calcium carbonate in the experiment, was confirmed by another experiment in which kaolin was replaced by a definitely acid clay soil.

In another set of pot cultures, the artificial soil media were replaced by two natural soils, one a poor acid sand and the other a fertile loam. Vanillin was used as the toxic agent, and the results showed that whereas it had a decidedly depressing influence on growth in the poor sand when neither fertilisers nor lime were added, it had no effect when used on the good soil.

Summarising the results of the investigation, it is clear that chemical factors played an important part in counteracting the effect of plant toxins in the soil.

L. M. U.

The Effect of Soil Reaction on the Availability of Ammonium Sulphate. R. C. COOK and F. E. ALLISON (*Soil Sci.*, 1917, 3, 487—498).—A study of the effect of the application of increasing amounts of calcium oxide on three types of soil, a sand, a sandy loam, and a silt loam, having lime requirements respectively of 1360 kilos., 1360 kilos., and 1818 kilos. of calcium oxide per acre, either with or without the application of ammonium sulphate. Pot experiments were carried out, the crop grown being buckwheat. Small applications of calcium oxide produced practically as large crop yields as where enough was applied to neutralise the soil or to make it distinctly alkaline, the beneficial effects of calcium oxide on acid soils being more marked on the sandy soils than on the silt loam. On the more acid soils, although the crop was smaller, it usually contained a higher percentage of nitrogen, the recovery of nitrogen, where

applied, being, in many cases, as great from the acid soils as from the alkaline soils. Buckwheat is able to utilise the nitrogen applied as ammonium sulphate, from soils having lime requirements of 1360—1818 kilos. per acre. W. G.

The Significance of Sodium Salts for Plant Growth and the Application of Salt as Manure. E. BLANCK (*Fühling's Landw. Zeit.*, 1916, 65, 441; from *Bied. Zentr.*, 1917, 46, 271—272).—A general survey of the present position as to the value of sodium salts for plant nutrition. Sodium is not an indispensable plant constituent, and cannot replace potassium in the true sense of the term. It is stated, however, that a partial replacement is possible, and, in fact, appears to occur.

The value of applications of common salt for certain plants rests on an indirect effect, inasmuch as sodium salts act as ballast and minimise the risk of the plants suffering from "ash starvation." Sodium appears to be especially suitable for this purpose, as it not only facilitates the absorption of potash, but is also of importance for the translocation of the latter constituent in the plant.

Applications of common salt may induce undesirable changes in the physical condition of some soils, whilst in others they ensure a better utilisation of the soil potash compounds. H. B. H.

Gypsum as a Fertiliser. OTTO NOLTE (*J. Landw.*, 1917, 65, 67—73).—The literature of this subject is discussed, and the following conclusions are drawn. Gypsum acts on the soil by means of both of its constituents, double decomposition occurring with the mineral compounds of the soil. Owing to its ability to undergo hydrolytic decomposition into acid and base, it influences the reaction of the soil especially by virtue of the constituent with the predominating reaction, that is, the sulphuric acid. Consequently, as far as possible, gypsum should not be used with acid and physiologically acid fertilisers, and in particular should never be applied to acid soils. On the other hand, it acts favourably in conjunction with physiologically basic salts, as it removes or weakens the basic reaction resulting from plant growth, and so assists in the retention of a loose texture by the soil. Gypsum may be employed with advantage when there is a shortage of such physiologically active fertilisers as potassium sulphate and chloride, superphosphate, and ammonium sulphate. T. H. P.

Dissolved Oxygen in Rain-water. ERIC HANNAFORD RICHARDS (*J. Agric. Sci.*, 1917, 8, 331—337).—Rain-water is very nearly saturated with oxygen when its temperature, as collected, is below 15°. During the summer months, when the temperature of the rain is above 15°, the dissolved oxygen is always less than the saturation quantity, sometimes by as much as 25 per cent. With normal clean rain-water there is no absorption of oxygen in twenty-four hours. Rain-water, like tap-water, if it is not shaken can become strongly supersaturated, owing to rise in temperature, without loss of oxygen. W. G.

Organic Chemistry.

Dissociation and Rearrangement of *iso*- and *tert*-Butyl Bromides in the Gaseous State at High Temperatures, and their Formation from Hydrogen Bromide and *iso*Butene.

R. F. BRUNEL (*J. Amer. Chem. Soc.*, 1917, 39, 1978—2005. Compare A., 1911, i, 413; ii, 974).—An investigation of the equilibrium between *isobutyl* and *tert*-butyl bromides and their dissociation products, *isobutene* and hydrogen bromide, at 221° and 275°. It is shown how the dissociation constant for the mixture of bromides at equilibrium may be calculated, and from the results of experiments with the vapour of each bromide the average values 0.0490 and 0.00992 (for mols. per litre) are obtained for the temperatures 275° and 221° respectively.

In the dissociation of these bromides and also in their formation from *isobutene* and hydrogen bromide, catalytic influences are active; in the absence of liquid bromide, the hydrocarbon combines only slowly with hydrogen bromide, and under these conditions *isobutyl* bromide is generally formed in addition to the tertiary compound. On the other hand, in the presence of either liquid bromide the combination proceeds much more rapidly, and unexpectedly gives rise only to the tertiary bromide.

From a knowledge of the above dissociation constant at 275°, the assumption that on cooling the equilibrium mixture of vapours yielded by *isobutyl* bromide or *tert*-butyl bromide to the ordinary temperature the *isobutene* present passes entirely into the *tert*-butyl compound, and a knowledge of the composition of the condensed liquid, it is calculated that at the temperature stated 80.0% of the undissociated bromide in the equilibrium mixture exists in the form of the tertiary compound. The values for the dissociation constants of the bromides at the two temperatures stated also enables the calculation of the heat of addition of hydrogen bromide to *isobutene* with production of the equilibrium mixture of bromides, the result being 15,886 cal.

D. F. T.

The Action of Phosphoryl Chloride on Methyl or Ethyl Alcohol. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1917, 99, 187—189).

—The calculated quantity of the alcohol is added drop by drop to the phosphoryl chloride, cooling in a freezing mixture. When the mixture is gently warmed, hydrogen chloride and methyl or ethyl chloride are evolved. The residue consists of alkyl metaphosphate, part of which is soluble and part insoluble in chloroform, the insoluble ester being probably a polymeride. The action may be represented by the equations: $\text{POCl}_3 + 2\text{EtOH} = 2\text{HCl} + \text{POCl}(\text{OEt})_2$; $\text{POCl}(\text{OEt})_2 = \text{EtCl} + \text{EtPO}_3$.

C. H. D.

b b

Esterification. IX. The Esterification of Acetic and Propionic Acids by Methyl, Ethyl, Propyl, *iso*Butyl, and *iso*Amyl Mercaptans. EDGAR M. FABER and E. EMMET REID (*J. Amer. Chem. Soc.*, 1917, **39**, 1930—1938. Compare Reid and others, A., 1910, i, 481; 1915, i, 885; this vol., i, 89).—In extension of the earlier researches, it is found that at 200° the limit of esterification for a mercaptan is much lower than that for the corresponding alcohol, the proportions of the reacting substances apparently having little influence on the limit, which is generally attained under ninety-six hours. With increase in molecular weight of the mercaptans there is a gradual reduction in the final quantity of product, and the limits are also found to be somewhat lower for propionic than for acetic acid. The mercaptan esters of higher molecular weight show somewhat greater tendency to decomposition with formation of hydrogen sulphide under the conditions of the experiments. D. F. T.

Method for Fractionating Fats and Oils. ARMIN SEIDENBERG (*J. Ind. Eng. Chem.*, 1917, **9**, 855—858).—The oil or fat is dissolved in a mixture of two or more solvents (for example, ether and alcohol), one or more of which is more volatile and exerts a greater solvent action on the glycerides. This solvent is first removed gradually by aspirating air through the solution, later the remaining solvent is removed in the same way. Owing to the slow decrease in temperature due to the evaporation, and to the gradual removal of the solvents, the various glycerides are precipitated in the order of their solubility. The various fractions are separated by filtration, and each is again treated as described as often as is necessary to obtain a pure product. W. P. S.

Action of Nitric Acid on Castor Oil. R. BRIGHTMAN (*J. Soc. Chem. Ind.*, 1917, **36**, 984—986).—Castor oil reacts very energetically with a mixture of nitric and sulphuric acids; the violence of the action is largely due to the latter acid, and is avoided when it is replaced by glacial acetic acid. The oil is readily nitrated by dilute nitric acid. The nitrated castor oil obtained by the latter method is a reddish-brown, viscid oil with a characteristic odour. It dissolves readily in acetone, ether, alcohol, or acetic acid, but is insoluble in carbon disulphide. It has D about 1.05. It does not decompose at 100°, but slowly darkens when preserved in a warm place.

The usual analytical methods are only applicable with difficulty to the nitrated oil, and it is best characterised by estimating the nitrogen content by Kjeldahl's method. The saponification number varied in a number of samples from 280 to 340; the iodine number was about 4 to 5, but one sample gave 14.9. The iodine number of the fatty acids varied from 18.8 to 25.3. The nitrogen content varied between 2.3 and 3.8%, but was usually about 3%. The percentage of ash was less than 0.05.

Apparently, the nitrated castor oil is formed from castor oil as the result of two simultaneous processes of nitration and oxidation, and thus probably consists of the triglycerides of the nitric ester of

oxidised ricinoleic acid. With this view its nitrogen content is in close agreement.

H. W.

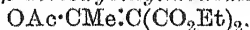
Complex Salts. The Preparation of Potassium Iridotrioxalate and the Optical Resolution of the Iridotrioxalates.

MARCEL DELÉPINE (*Bull. Soc. chim.*, 1917, [iv], 21, 157—172).—A more detailed account of work already published (compare A., 1914, i, 1048).

W. G.

Constitution of Mono- and Di-acylmalonic Esters, and of Diacetylacetone. KARL VON AUWERS and ELISABETH AUFFENBERG (*Ber.*, 1917, 50, 929—952).—It is usual to assume that when β -diketones or β -ketonic esters change into enols, the hydrogen of the new hydroxyl group is drawn from the methylene group which is between the carbonyl groups. Brühl, however, showed that ethyl diacetylmalonate corresponds in its optical properties more closely with an enol of the formula $[\text{CH}_2\text{:C}(\text{OH})]_2\text{C}(\text{CO}_2\text{Et})_2$, and that ethyl acetylmalonate may be represented perhaps by the formula $\text{CH}_2\text{:C}(\text{OH})\cdot\text{CH}(\text{CO}_2\text{Et})_2$ (A., 1894, ii, 434). Bielecki and Henri (A., 1914, ii, 319) have also assigned an abnormal constitution, represented by $\text{CH}_2\text{Ac}\cdot\text{C}(\text{OH})\text{:CH}_2$, to acetylacetone. The present authors have now examined these compounds, both optically and chemically, and new light is thrown on their constitutions.

CONSTITUTION OF "ETHYL DIACETYL MALONATE."—The objections to Brühl's formula are that it does not explain why the ester is insoluble in alkali hydroxides, does not react with ferric chloride, and readily loses an acetyl residue by hydrolysis. The true explanation is that the compound is really the *O*-acetate of enolic ethyl acetylmalonate [*ethyl β -acetoxyethylidenemalonate*] (1),



The best way to prepare the substance is actually by acetylating the monoacetylmalonate in pyridine solution. Furthermore, different products are obtained when ethyl acetylmalonate is propionylated and ethyl propionylmalonate is acetylated, namely, *ethyl β -propoxyethylidenemalonate* (2) and *ethyl β -acetoxypropylidenemalonate* (3) respectively. Similarly, *ethyl β -propoxypropylidenemalonate* (4), $\text{C}_2\text{H}_5\cdot\text{CO}_2\cdot\text{CEt}\text{:C}(\text{CO}_2\text{Et})_2$, may be prepared. These esters are hydrolysed even by phenylhydrazine, the acyl residues being transferred to this base. Finally, compounds of this type contain the grouping $\text{—C}\text{:C}\text{:C}\text{:O}$, which is associated with pronounced optical exaltations. The values of the molecular refractions and dispersions actually found are greater than those calculated for such esters with three carbonyl groups and an ethylenic linking by expected amounts.

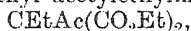
For comparison, the properties of these esters are tabulated together. Full data are recorded in the original.

Ester.	B.p. 15 mm.	D_4^{20} .	n_D^{20} .	E_{Σ_a} .	E_{Σ_b} .	$E_{\Sigma_b} - \Sigma_a$.	$E_{\Sigma_c} - \Sigma_a$.
1	154°	1.113	1.4500	+0.58	+0.59	+22%	+20%
2	160	1.097	1.4513	0.49	0.50	21	22
3	156	1.095	1.4506	0.50	0.51	19	20
4	162	1.078	1.4507	0.44	0.44	19	18

b b 2

CONSTITUTION OF ETHYL ACETYLMALONATE.—Ethyl acetylmalonate is best prepared by the action of ethyl chloroformate on ethyl cuproacetoacetate. Its b. p., under 19 mm., fluctuates between 118° and 129°, which may be due to a difference in b. p. between the ketonic and enolic forms.

The optical properties of this ester clearly point to the presence in the molecule of a conjugated system, which is, of course, suggested also by the acylations described above. The ester (5) is, therefore, an enol of the ordinary type, $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{CO}_2\text{Et})_2$, and so is ethyl propionylmalonate (6). There is also chemical evidence in support of this. Ethyl sodioacetylmalonate is very indifferent to the action of alkyl haloids, but the small amount of alkyl derivative which is obtained under strenuous conditions can be shown to be an α -alkyl compound. Although ethyl acetylethylmalonate (7),

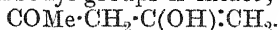


cannot be obtained readily by ethylating the acetylmalonate, it can be obtained by acetylating ethyl ethylmalonate. Furthermore, the same *ethyl α -chloroacetylmalonate* (8), $\text{CClAc}(\text{CO}_2\text{Et})_2$, is obtained by the action of sulphuryl chloride on free ethyl acetylmalonate, and by the action of chlorine on the copper salt of this ester. Both specimens are alike in physical and optical properties, both are stable towards alkalis, permanganate, and bromine, and both yield a *compound*, probably of the formula $\text{CMe}\cdot\text{C}(\text{CO}_2\text{Et})_2$
 $\text{N} \begin{array}{c} \text{||} \\ \text{---} \end{array} \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ (silky, orange-coloured needles, m. p. 81°), when treated with *p*-nitrophenylhydrazine. *Ethyl α -bromoacetylmalonate* (9) can also be obtained from the copper salt.

The principal properties of the esters mentioned in this section are given in the following table:

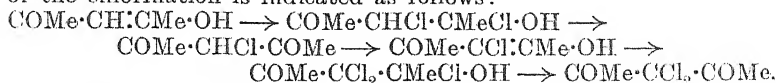
Ester.	B.p. 15/mm.	D_4^{20}	n_D^{20}	E_{Σ_a}	E_{Σ_b}	$E_{\Sigma_\beta} - \Sigma_a$	$E_{\Sigma_\gamma} - \Sigma_a$
5	120°	1.100	1.447	+0.95	+0.97	+44%	+46%
6	138	1.076	1.442	0.67	0.67	27	28
7	130	1.054	1.434	0.24	0.23	1	1
8	132	1.187	1.441	0.31	0.30	4	2
9	144	1.388	1.459	0.24	0.23	7	5

CONSTITUTION OF ACETYLACETONE.—As against much evidence in support of a formula of the usual type, $\text{COMe}\cdot\text{CH}\cdot\text{CMe}\cdot\text{OH}$, for acetylacetone, the authors have been unable to find more than one fact on record which would favour the view that the methylene group between the carbonyl groups is intact; thus,



This is the fact that acetylacetone yields hexachloro- and hexabromoderivatives which readily give trihalogenoacetones, the former being represented, therefore, by the formula $\text{CX}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CX}_3$ (Combes, A., 1888, 666). Combes also described, however, a mono- and a di-chloro-derivative of acetylacetone, and it is obvious from their properties that the halogen atoms are attached to the central carbon atom, thus, $\text{COMe}\cdot\text{CCl}_2\cdot\text{COMe}$ (A., 1890, 1394). Further

evidence in support of this view is now adduced, and the mechanism of the chlorination is indicated as follows:

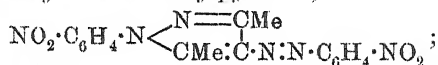


It is suggested that the dihalogeno-derivative is formed in this normal way even in the extreme cases, the hexa-derivatives being produced after internal rearrangement.

Chloroacetylacetone, $\text{COMe}\cdot\text{CCl}\cdot\text{COMe}\cdot\text{OH}$, has b. p. $153-154^\circ$, D_4^{20} 1.165, n_D^{20} 1.4783, $E\Sigma_a + 1.01\%$, $E\Sigma_D + 1.08\%$, $E\Sigma_\beta - E\Sigma_a + 86\%$, calculated for the enolic form; dichloroacetylacetone,

$\text{COMe}\cdot\text{CCl}_2\cdot\text{COMe}$, has b. p. $79^\circ/11$ mm., D_4^{20} 1.303, n_D^{20} 1.4574, $E\Sigma_a + 0.18\%$, $E\Sigma_D + 0.17\%$, $E\Sigma_\beta - E\Sigma_a + 2\%$, $E\Sigma_\gamma - E\Sigma_\beta + 2\%$, calculated for the ketonic form; bromoacetylacetone, $\text{COMe}\cdot\text{CBr}\cdot\text{COMe}\cdot\text{OH}$, has b. p. $96^\circ/13$ mm., irritates the eyes, and quickly becomes dark coloured in the air.

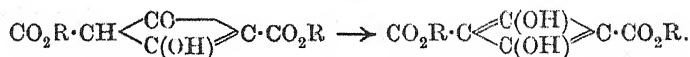
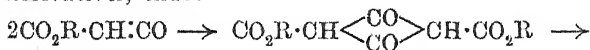
Dichloroacetylacetone reacts with *p*-nitrophenylhydrazine hydrochloride to form a compound which may also be prepared by converting acetylacetone into *p*-nitrobenzeneazoacetylacetone (Bülow and Schlotterbeck, A., 1902, i, 649) and treating this with *p*-nitrophenylhydrazine. The compound is, therefore, 4-*p*-nitrobenzene-azo-1-*p*-nitrophenyl-3:5-dimethylpyrazole,



it crystallises in orange-coloured needles, m. p. $236-238^\circ$.

J. C. W.

Ketens. XXVI. Ketenmonocarboxylic Esters. II. STAUDINGER and H. BECKER (*Ber.*, 1917, 50, 1016—1024. Compare A., 1914, i, 285).—Researches on ketens have revealed the facts that mono-substituted ketens are extremely unstable, and that carboxyl groups enhance the tendency of these compounds to form polymers. It was therefore expected that attempts to isolate ketenmonocarboxylic esters would result in the formation of cyclobutane derivatives, thus:



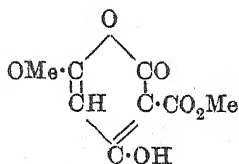
When, in the normal way, methyl and ethyl bromomalonyl chlorides were treated with zinc, practically no definite compounds could be obtained, whilst the alternative method for the production of ketens, namely, the action of quinoline on the ester-chlorides, did not give the hoped-for cyclobutane compounds, but pyrone derivatives. The polymerisation of the simple keten takes place in this case according to the scheme:



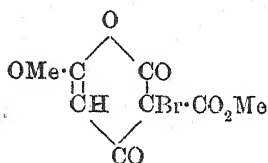
The pyrone derivatives are quite analogous to dehydracetic acid, the formation of which can likewise be traced to a polymerisation of the unknown acetylketen, thus:



Methyl malonyl chloride, prepared from thionyl chloride and potassium methyl malonate, has b. p. 57—59°, and decomposes to a certain extent into hydrogen chloride and the dimeric keten-carboxylate on distillation. It reacts with aniline to form *methyl malonanilate*, m. p. 42—43°, and with bromine to give *methyl bromomalonyl chloride*, $\text{CO}_2\text{Me}\cdot\text{CHBr}\cdot\text{COCl}$, b. p. 90—91°/10 mm. This yields *methyl bromomalonanilate*, m. p. 113—114°, and reacts with zinc to give a very small quantity of a compound, $\text{C}_8\text{H}_8\text{O}_6$, m. p. 179—180°, which behaves like a dibasic acid. Methyl malonyl chloride reacts with quinoline to form *methyl 4-hydroxy-6-methoxy-1:2-pyrone-3-carboxylate* (annexed formula), which crystallises in needles, m. p. 148—150°, and is decomposed by hot water into methyl malonate, malonic and acetic acids, and methyl acetoacetate (*semicarbazone*, m. p. 151—152°). This ester also

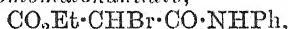


reacts with ammonia



to form malonamide, with aniline to give malonanilide, and with bromine to give the compound (annexed formula), decomp. 180—185°.

Ethyl malonyl chloride, b. p. 63—64°/10 mm., may be converted into *ethyl malon-p-toluidate*, m. p. 83°, *ethyl bromomalonyl chloride*, b. p. 88—90°/10 mm., *ethyl bromomalonanilate*,



m. p. 94°, and also *ethyl 4-hydroxy-6-ethoxy-1:2-pyrone-3-carboxylate*, m. p. 85—86°. J. C. W.

Ketens. XXVII. Ethyl Ketendicarboxylate and Methyl Phenylketencarboxylate. H. STAUDINGER and H. HIRZEL (*Ber.*, 1917, 50, 1024—1035. Compare this vol., i, 178).—The three ketencarboxylates, ethyl ethylketencarboxylate (A., 1910, i, 89), ethyl ketendicarboxylate, and methyl phenylketencarboxylate, have many unexpected properties. In the first place, they are much paler in colour than the corresponding simple ketens, or oxomalonates, of somewhat similar structure. Thus, ethyl ketendicarboxylate, $\text{CO}:\text{C}(\text{CO}_2\text{Et})_2$, is colourless, whereas diethylketen, $\text{CO}:\text{C}(\text{C}_2\text{H}_5)_2$, and ethyl oxomalonate, $\text{CO}(\text{CO}_2\text{Et})_2$, are yellow. Furthermore, they are remarkably stable towards oxygen, even at higher temperatures, but in other respects they are highly reactive. They polymerise very readily to cyclobutanedione derivatives, but at widely different rates, and altogether they show how little can be predicted about the influence of a particular group on the reactivity of a compound.

In the cases of carbonyl compounds and ethylenes there are also perplexing irregularities in colour and tendency to polymerise. A table illustrating this feature is given.

Ethyl ethylketencarboxylate gradually decomposes at 200° into ethyl malonate and resins, and is completely polymerised after about forty minutes.

Methyl phenylketencarboxylate reacts with water to form methyl hydrogen phenylmalonate, m. p. 95°, and with aniline to yield *methyl phenylmalonanilate*, m. p. 109°, or with *p*-toluidine to form *methyl phenylmalon-p-toluidate*, m. p. 148—149°. It polymerises at 30° within about two days, giving methyl 1:3-diketo-2:4-diphenylcyclobutane-2:4-dicarboxylate. This ester is readily depolymerised to the keten at 150°, whilst it reacts with water to form *methyl diphenylacetonedicarboxylate*, $\text{CO}(\text{CHPh}\cdot\text{CO}_2\text{Me})_2$, m. p. 90—91°.

Ethyl ketendicarboxylate absorbs water from the air and deposits crystals of diethyl hydrogen methanetricarboxylate, which decompose in a few seconds into ethyl malonate and carbon dioxide. It reacts with alcohol to form ethyl methanetricarboxylate, and with aniline to form diethyl methanetricarbonanilide, whilst it changes gradually at 180° into ethyl methanetricarboxylate and a highly fluorescent resin. At 30° it is by no means completely polymerised, even after one hundred days, and at 100° it takes several days to effect polymerisation. The viscous, yellow polymeride, ethyl 1:3-diketocyclobutanetetracarboxylate, is depolymerised at 150°, and reacts with water to form *ethyl acetonetetracarboxylate*, $\text{CO}[\text{CH}(\text{CO}_2\text{Et})_2]_2$, which has b. p. 95—102°/0.3 mm., and behaves on titration as a weak, monobasic acid. J. C. W.

Relation between the Configuration and Rotation of Epimeric Monocarboxylic Sugar Acids. III. Phenylhydrazides. P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1917, 31, 623—626. Compare A., 1916, ii, 545).—Comparison of the rotations of the phenylhydrazides of the various sugar acids, including gluconic, mannonic, galactonic, allonic, and arabonic acids, indicates that the magnitude of the rotation of the α -carbon atom is not altogether constant even for the series of phenylhydrazides, but the rule of the relation of direction of the rotation to the configuration of the α -carbon atom remains valid. H. W. B.

Influence of Different Compounds on the Destruction of Monosaccharides by Sodium Hydroxide and on the Inversion of Sucrose by Hydrochloric Acid. Constitutional Formula of α -Amino-acids and of Betaine. H. I. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, 20, 88—96. Compare A., 1913, ii, 887; this vol., i, 195).—Glycine and alanine both retard the destructive action of sodium hydroxide on galactose, as they do on dextrose (*loc. cit.*). They also retard the inversion of sucrose by hydrochloric acid. Phenol also retards the action of the alkali on dextrose, but has no influence on the inversion of sucrose. Betaine does not influence the action of sodium hydroxide on dex-

trose, but retards the inversion of sucrose by acid. From these results the author draws the conclusion that glycine and alanine are best represented by the usual straight-chain formula when in alkaline or acid solution, and that betaine is best represented by the cyclic formula, $\text{CO} \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{NMe}_3$, in neutral and alkaline solutions and by the straight-chain formula, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{NMe}_3\text{Cl}$, in acid solution. W. G.

Preparation of Lyxose. E. P. CLARK (*J. Biol. Chem.*, 1917, 31, 605—607).—A detailed description of the preparation of lyxose on a large scale by the oxidation of calcium *D*-galactonate by means of hydrogen peroxide, using ferric acetate as a catalyst (compare Ruff and Ollendorff, A., 1900, i, 476). H. W. B.

Methylation by means of Formaldehyde. I. Mechanism of the Interaction of Formaldehyde and Ammonium Chloride. The Preparation of Methylamine and Dimethylamine. EMIL ALPHONSE WERNER (T., 1917, 111, 844—853).—Brochet and Cambier have described the most favourable conditions for the production of methylamine hydrochloride by the interaction of formaldehyde and ammonium chloride (A., 1895, i, 325), and Knudsen (A., 1915, i, 220) has shown how dimethylamine and trimethylamine can be obtained as well in other circumstances. In discussing the mechanism of the reactions, it was assumed by these workers, in each case, that complex condensation products of formaldehyde and ammonia are the precursors of the methylamines, but it is now shown that a much simpler explanation is more probable.

The clue was found in an examination of the distillates obtained by heating mixtures of formalin (containing methyl alcohol, as usual) with ammonium chloride, methylamine hydrochloride, and dimethylamine hydrochloride. The noteworthy products in the first two cases were methyl formate and carbon dioxide, which shows that much formic acid is developed during the reaction. The series of changes is expressed by the following equations: (1) $\text{H} \cdot \text{CHO} + \text{NH}_3(\text{HCl}) = \text{H}_2\text{O} + \text{CH}_3\text{NH}(\text{HCl})$; (2) this + $\text{H}_2\text{O} + \text{H} \cdot \text{CHO} = \text{CH}_3\text{NH}_2\text{HCl} + \text{H} \cdot \text{CO}_2\text{H}$. The brackets, thus, $\text{NH}_3(\text{HCl})$, are used to indicate highly dissociated salts. The formic acid is then partly esterified, but mainly oxidised to carbon dioxide and water.

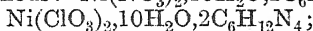
(3) $\text{CH}_3\text{O} + \text{CH}_3\text{NH}_2(\text{HCl}) = \text{H}_2\text{O} + \text{CH}_3\text{NMe}(\text{HCl})$; (4) this + $\text{H}_2\text{O} + \text{H} \cdot \text{CHO} = \text{NHMe}_2\text{HCl} + \text{H} \cdot \text{CO}_2\text{H}$; (5) $\text{CH}_3\text{O} + 2\text{NHMe}_2(\text{HCl}) = \text{H}_2\text{O} + \text{CH}_3(\text{NMe}_2)_2\text{HCl}$; (6) this = $\text{NMe}_3\text{HCl} + \text{CH}_3\text{NMe}(\text{HCl})$; and, finally, in the absence of sufficient formaldehyde, the base, CH_3NMe , would form the known trimeride (Brochet and Cambier). Naturally, reactions (2) to (4) overlap to a certain extent, but it is possible to separate the hydrochlorides of the bases easily by reason of the following facts: (a) ammonium chloride is practically insoluble in a concentrated solution of methylammonium chloride; (b) dimethylammonium chloride is

more soluble in water than methylammonium chloride, and the former is soluble in chloroform and the latter not. Trimethylamine (6) is only formed if the heating is prolonged or the temperature rises above 110° . Only polymerised condensation products like the base $(\text{CH}_3)_3\text{NMe}$ give precipitates with picric acid, and no such precipitates can be obtained during the earlier stages of the reaction.

Details are given for the preparation of the methylamine and dimethylamine salts on a considerable and economical scale.

J. C. W.

Isomorphism of Nitrates and Chlorates. RENZO REA (*Gazzetta*, 1917, 47, ii, 69—86).—The following compounds are completely isomorphous: $\text{Ni}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$;



$\text{Co}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$; $\text{Co}(\text{ClO}_3)_2 \cdot 10\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$. The compound of magnesium chlorate and hexamethylenetetramine is isodimorphous with the compound of magnesium nitrate and hexamethylenetetramine. The corresponding cadmium salts are probably also isodimorphous.

The following crystallographic measurements are recorded: $\text{Ni}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ is triclinic [$a:b:c = 1.0265:1.0.9646$; $\alpha = 60^{\circ}36'$, $\beta = 75^{\circ}29'$, $\gamma = 78^{\circ}20'$]. $\text{Ni}(\text{ClO}_3)_2 \cdot 10\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ is triclinic [$a:b:c = 1.0392:1.0.9732$; $\alpha = 60^{\circ}55'$, $\beta = 77^{\circ}15'$, $\gamma = 77^{\circ}7'$].

$\text{Co}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ is triclinic [$a:b:c = 1.0136:1.0.9590$; $\alpha = 60^{\circ}30'$, $\beta = 75^{\circ}33'$, $\gamma = 77^{\circ}58'$]. $\text{Co}(\text{ClO}_3)_2 \cdot 10\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ is triclinic [$a:b:c = 1.0192:1.0.9636$; $\alpha = 60^{\circ}34'$, $\beta = 75^{\circ}38'$, $\gamma = 78^{\circ}17'$].

$\text{Mg}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ is rhombic [$a:b:c = 0.8388:1:0.4894$]. $\text{Mg}(\text{ClO}_3)_2 \cdot 10\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ is triclinic [$a:b:c = 1.0240:1.0.9692$; $\alpha = 60^{\circ}16'$, $\beta = 76^{\circ}33'$, $\gamma = 77^{\circ}11'$].

$\text{Cd}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$ is monoclinic [$a:b:c = 1.1006:1:1.1360$; $\beta = 49^{\circ}45'$]. $\text{Cd}(\text{ClO}_3)_2 \cdot 5\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$ is monoclinic [$a:b:c = 1.0221:1.0.9764$; $\beta = 42^{\circ}45'$].

R. V. S.

Chondrosamine and its Synthesis. P. A. LEVENE (*J. Biol. Chem.*, 1917, 31, 609—621. Compare A., 1916, i, 712, 713).—The author brings forward conclusive evidence of the identity of natural chondrosamine and synthetic lyxohexosamine. All the derivatives prepared from chondrosamine have now been obtained from synthetic lyxohexosamine. The difference between the rotations of chondrosamine hydrochloride, $[\alpha]_D + 129^{\circ}$ (initial) and $+95^{\circ}$ (equilibrium) (Levene and La Forge, A., 1914, i, 889) and of lyxohexosamine hydrochloride, $[\alpha]_D + 53^{\circ}$ (initial) and $+94.2^{\circ}$ (equilibrium) (Levene, *loc. cit.*), is shown to be due to the fact that the substance exists in two epimeric forms. The conditions for the isolation of either form have not been entirely elucidated, but natural chondrosamine has been obtained in both forms, one of which is identical with that in which the synthetic lyxohexosamine has so far always been obtained.

b b*

Lyxohexosaminic acid prepared from lyxosimine and hydrocyanic acid (Levene and La Forge, A., 1915, i, 944) is shown also to exist in two epimeric forms, which accounts for the variation in the rotations of different preparations of the synthetic acid. The lyxohexosamine obtained by reduction of lyxohexosamic acid yields, on oxidation with mercuric oxide by Pringsheim and Ruschmann's method (A., 1916, i, 506), a mixture of epimeric lyxohexosamic acids which is identical with the chondrosamic acid prepared from chondrosamine.

Both natural and synthetic hexosamines on oxidation with bromine yield the same *aa'*-anhydrotalonic acid, which, on further oxidation with nitric acid, produces an optically active anhydrotetrahydroxyadipic acid. When chondrosamic acid is deaminised, it yields anhydrogalactonic acid, which, on treatment with nitric acid, gives an optically inactive anhydrotetrahydroxyadipic acid. The synthetic lyxohexosamic acid yields the same products as the hexosamines. Since the synthetic acid is a mixture of two epimerides, one being chondrosamic acid, the inactive anhydrotetrahydroxyadipic acid must be anhydromucic acid, whilst the optically active acid must be anhydrotalomucic acid.

Chondrosamine and the synthetic lyxohexosamine also yield identical penta-acetates (compare Hudson and Dale, A., 1916, i, 597), both α - and β -forms being isolated. H. W. B.

Separation of Glutamic Acid from other Amino-acids.

A. CORTI (Brit. Pat., 106081, 1916; from *J. Soc. Chem. Ind.*, 1917, 36, 979).—The acid solution obtained after hydrolysis of albumins is filtered hot, and then sufficient alkali or alkaline-earth hydroxide or carbonate is added to neutralise both the free hydrochloric acid and that combined with the amino-acid, leaving the latter unaffected. When the liquid has cooled and remained for some days, the glutamic acid is separated by filtration or by centrifugal action, and purified from resinous matter by crystallisation from water and decolorised with charcoal. Other amino-acids can be obtained by treatment of the mother liquors.

H. W.

Synthesis of β -Ketonic Bases. C. MANNICH (*Arch. Pharm.*, 1917, 255, 261—276).— β -Ketonic bases are obtained by the reaction between acetone or diethyl ketone, 35% formaldehyde solution and ammonium salts, or, yet more readily, the hydrochloride of methyl- or dimethyl-amine. Thus by boiling a solution of 35% formaldehyde (1 mol.), dimethylamine hydrochloride (1 mol.), and acetone (5 mols.) for twelve hours, the hydrochloride, a very hygroscopic, crystalline salt, of δ -dimethylaminobutan- β -one, b. p. 50—52°/13 mm., is obtained; the *aurichloride* forms needles, m. p. 124—126°. By a similar reaction with methylamine hydrochloride several bases are formed which are difficult to separate, but *methyl-di- γ -ketobutylamine*, $\text{NMe}(\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe})_2$, has been isolated, which forms crystals, m. p. 132°, and yields a *picrate*, yellow

needles, *platinichloride*, orange-red prisms, and *aurichloride*, yellow prisms, m. p. 153° (decomp.).

The reaction between acetone, 35% formaldehyde, and ammonium chloride at the ordinary temperature for five weeks yielded a number of condensation products, but no individual constituent could be isolated.

When diethyl ketone is used in place of acetone, dimethylamine hydrochloride yields only α -dimethylamino- β -methylpentan- γ -one, $\text{COEt}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NMe}_2$, b. p. 59—61°/10 mm. (*hydrochloride*, m. p. about 105°; *aurichloride*, golden-yellow prisms, m. p. 71°), but methylamine hydrochloride yields five products, the quantities of which vary with the experimental conditions, (1) β -methyl- Δ^2 -penten- γ -one, $\text{CH}_2\cdot\text{CMe}\cdot\text{COEt}$, b. p. 117—119°/760 mm. (*semicarbazone*, leaflets, m. p. 158—159°); (2) α -methylamino- β -methylpentan- γ -one, $\text{NHMe}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{COEt}$, b. p. 72—74°/13 mm. (*platinichloride*, orange-yellow crystals, m. p. 146—147°); (3) 1:3:5-trimethyl-4-piperidone, $\text{NMe}\cdot\left\langle\begin{array}{c} \text{CH}_2\cdot\text{CHMe} \\ \text{CH}_2\cdot\text{CHMe} \end{array}\right\rangle\text{CO}$, which is isolated as the *hydrochloride*, $\text{C}_8\text{H}_{15}\text{ON}\cdot\text{HCl}$, prisms, m. p. about 235° (decomp.) (*platinichloride*, orange-yellow prisms, m. p. 204°; *hydrochloride* of the *oxime*, $\text{C}_8\text{H}_{16}\text{ON}_2\cdot\text{HCl}$, m. p. 191—192°); (4) $\alpha\epsilon$ -dimethylamino- $\beta\delta$ -dimethylpentan- γ -one, $\text{CO}(\text{CHMe}\cdot\text{CH}_2\cdot\text{NHMe})_2$, or $\beta\beta$ -dimethylaminomethylpentan- γ -one, $\text{COEt}\cdot\text{CMe}(\text{CH}_2\cdot\text{NHMe})_2$, b. p. 112—113°/13 mm., which forms a slowly crystallising *hydrochloride*, *aurichloride*, golden-yellow rosettes, *picrate*, *platinichloride*, orange-yellow crystals, and the *hydrochloride* of the *oxime*, $\text{C}_9\text{H}_{21}\text{ON}_3\cdot 2\text{HCl}\cdot\text{H}_2\text{O}$, large prisms, m. p. 188—190° (decomp.), and (5) methyl-di- γ -keto- β -methylamylamine, $\text{NMe}(\text{CH}_2\cdot\text{CHMe}\cdot\text{COEt})_2$, b. p. 147—150°/14 mm. (apparently with decomp.) (*hydrochloride*, very hygroscopic crystals, m. p. 104—106°; *methiodide*, crystals, m. p. 139°, and the *hydrochloride* of the *dioxime*,

$\text{C}_{13}\text{H}_{27}\text{O}_2\text{N}_3\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$, crystals, m. p. 192° [decomp.]).

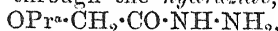
The reaction between 35% formaldehyde, ammonium chloride, and diethyl ketone at the b. p. yields several products, the only substance which could be isolated being 1:3:5-trimethyl-4-piperidone.

C. S.

The Special Reactions in the Transformation of the Azides of the Carboxylic Acids. VII.—XIII. THEODOR CURTIUS (*J. pr. Chem.*, 1917, [ii], 95, 168—256. Compare *ibid.*, 1916, 94, 273).—[With BERNHARD VAN DER LAAN.]—VII. *Hydrazides and Azides of the Alkyl Ethers of Glycollic Acid*.—Ethyl ethoxyacetate, $\text{OEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, b. p. 52°/12 mm., n_D^{20} 1.404, was obtained by the action of ethyl diazoacetate on ethyl alcohol in the presence of a little sulphuric acid; it forms a *hydrazide*, $\text{OEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, leaflets, m. p. 32° (*hydrochloride*, colourless crystals, m. p. 102—103° with decomp.; *benzylidene* compound, leaflets, m. p. 82°; *o*-*hydroxybenzylidene* derivative, needles, m. p. 99—100°), and with ethyl acetoacetate yields 3-methylpyrazolone; the former product, on treatment with sodium nitrite and

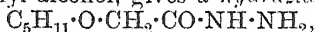
the calculated amount of hydrochloric acid, undergoes conversion into *ethoxyacetylazide*, $\text{OEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_3$, a heavy, pungent, pale yellow oil; this, when warmed with water, gives *ethoxymethylurethane*, $\text{OEt}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, a pleasant-smelling, viscid mass, which reacts with hydrochloric acid, producing a hygroscopic, crystalline mass, probably the *hydrochloride* of the urethane. With *p*-toluidine in ethereal solution the azide yields *s-p-tolyethoxymethylcarbamide*, $\text{OEt}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, needles, m. p. 84° (decomp.).

Ethyl *n*-propoxyacetate, prepared similarly to the ethoxy analogue, was converted through the *hydrazide*,



an uncrystallisable syrup (*benzylidene* derivative, lustrous, colourless leaflets, m. p. 65° ; *m*-nitro*benzylidene* derivative, needles, m. p. 118 — 119°), into *n*-propoxyacetylazide, $\text{OPr}^n\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_3$, a pungent, pale yellow oil, which reacts with alcohol at 55° , giving *n*-propoxymethylurethane, $\text{OPr}^n\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, a viscid, yellow mass (*hydrochloride*, colourless crystals).

Ethyl isoamyloxyacetate, obtained by the interaction of ethyl diazoacetate and amyl alcohol, gives a *hydrazide*,

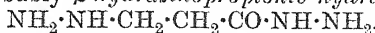


a viscous, yellow liquid, n_D^{18} 1.468 (*hydrochloride*, hygroscopic powder; *picrate*, yellow needles, m. p. 113° ; *benzylidene* derivative, m. p. 64° ; *p*-methyl*benzylidene* derivative, yellow powder, m. p. 77 — 5°), and an *azide*, $\text{C}_5\text{H}_{11}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_3$, a yellow, viscous oil of stupefying odour.

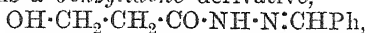
[With DAVID AUFHÄUSER.]—VIII. *Hydrazide and Azide of α - and β -Hydroxypropionic Acid*.—Ethyl lactate and hydrazine hydrate, when heated together for three to four hours, interact with formation of lactic hydrazide, $\text{OH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ (*hydrochloride*, m. p. 149° ; *benzylidene* compound, colourless crystals, m. p. 158° ; *salicylidene* derivative, yellow crystals, m. p. 169° ; *benzophenone* derivative, $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$, colourless prisms or needles, m. p. 158 — 159° ; *acetone* derivative, an unstable, uncrystallisable, yellow syrup; *ethyl acetoacetate* derivative, $\text{C}_9\text{H}_{16}\text{O}_4\text{N}_2$, pale yellow solid, decomp. near 200°). When kept for a long time, the viscous lactic hydrazide partly solidifies, giving a pasty mass containing the symmetrical *dilactic hydrazide*, $\text{N}_2\text{H}_2[\text{CO}\cdot\text{CHMe}\cdot\text{OH}]_2$, colourless, indistinct crystals, m. p. 151° . On careful treatment with sodium nitrite and hydrochloric acid, lactic hydrazide is converted into *lactic azide*, $\text{OH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{N}_3$, a pungent, yellow oil, which readily decomposes in moist air, giving acetaldehyde, ammonia, nitrogen, and carbon dioxide, and reacts with aniline, *p*-toluidine, and alcohol, yielding respectively lactanilide, lactotoluidide, and a mixture of acetaldehyde with ethyl allophanate.

Methyl β -hydroxypropionate, b. p. 177 — $184^\circ/746$ mm., D_4^{16} 1.105, obtained by the action of methyl iodide on the silver salt of the acid, is accompanied by a colourless liquid, b. p. 195 — $196^\circ/746$ mm., approximating to the composition $\text{C}_8\text{H}_{14}\text{O}_5$. The ethyl ester of β -hydroxypropionic acid reacts with hydrazine hydrate in alcoholic solution, giving a small quantity of a substance, silky scales,

decomp. near 240° without melting, which from its power of forming a *dibenzylidene* derivative, $C_{17}H_{18}ON_4$, m. p. near 240° (decomp.), is probably *β -hydrazinopropionic hydrazide*,

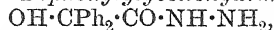


The reaction mixture from ethyl *β -hydroxypropionate* and hydrazine hydrate in aqueous solution, on evaporation, yields a yellow residue which must contain *β -hydroxypropionohydrazide*, because this product forms a *benzylidene* derivative,



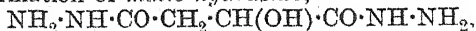
m. p. near 200° , and also on treatment with sodium nitrite and hydrochloric acid in the presence of ether gives rise to traces of *β -hydroxypropionic azide*.

[With ALFRED GOLDBERG.]—IX. *Hydrazide and Azide of Diphenylglycollic Acid*.—*Diphenylglycollohydrazide*,



needles, m. p. 168 — 169° , prepared by the action of hydrazine hydrate on an alcoholic solution of ethyl benzilate, forms a *hydrochloride*, m. p. 174 — 176° (decomp.), a *sodium* derivative, $C_{14}H_{13}O_2N_2Na$, m. p. near 158 — 160° , a *benzylidene* derivative, $C_{21}H_{15}O_2N_2$, needles, m. p. 198° , a *salicylidene* derivative, needles, m. p. 244 — 245° , an *acetone* derivative, $C_{17}H_{18}O_2N_2$, tablets, m. p. 190° , an *acetophenone* derivative, $C_{22}H_{20}O_2N_2$, needles, m. p. 180 — 181° , an *ethyl acetoacetate* derivative, $C_{20}H_{22}O_4N_2$, microscopic prisms, m. p. 114 — 115° , a *pyruvic acid* derivative, $C_{17}H_{16}O_4N_2$, needles, m. p. 197 — 198° , an *acetyl* derivative, $C_{16}H_{16}O_3N_2$, leafy crystals, m. p. 192 — 194° , and a *benzoyl* derivative, needles, m. p. 156 — 157° . In hot aqueous-alcoholic solution diphenylglycollohydrazide is converted by iodine into *bis-diphenylglycollohydrazide*, $N_2H_2[CO \cdot CPh_2 \cdot OH]_2$, colourless needles, m. p. 256 — 257° . *Diphenylglycollic azide*, $OH \cdot CPh_2 \cdot CO \cdot N_3$, obtained by the action of sodium nitrite on the aqueous solution of diphenylglycollohydrazide in the presence of acid, is an amorphous, resinous substance, which is decomposed by alcohol or water with formation of diphenylglycollamide and nitrogen; aqueous ammonia gives rise to a similar product, whilst in ethereal solution with *n*-propylamine, diethylamine, hydrazine hydrate, and phenylhydrazine respectively the analogous products are the *n*-propylamide, tablets, m. p. 80 — 82° , the *diethylamide*, needles, m. p. 95 — 96° , the *hydrazide* and the *phenylhydrazide*, needles, m. p. 139 — 141° , of diphenylglycollic acid; aniline and *p*-toluidine convert the azide into benzophenone, together with phenylcarbamide and *p*-tolylcarbamide respectively, whilst *m*-nitrobenzohydrazide yields benzophenone and *m*-nitrobenzoylsemicarbazide, needles, m. p. 202 — 203° .

[With CARL VON HOFER.]—X. *Hydrazide and Azide of Malic Acid*.—Ethyl malate reacts with hydrazine hydrate in alcoholic solution with formation of *malic hydrazide*,



an amorphous powder, m. p. 177.5° (*dihydrochloride*, needles, m. p. 189° (decomp.); *dibenzylidene* derivative, amorphous powder, m. p. 164° ; *cinnamylidene* derivative, microcrystalline powder, m. p. 192° ; *acetone* derivative, crystalline powder, m. p. 168°),

which by treatment with sodium nitrite solution in the presence of ether is convertible into *malic azide*, $\text{N}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{N}_3$, a pale yellow oil of characteristic odour; this is decomposed by alcohol with production of a yellow, oily *urethane* compound, which is decomposed by cold dilute acids with liberation of carbon dioxide and formation of aminoacetaldehyde.

[With CHRISTIAN OHLGART.]—XI. *Hydrazide and Azide of Tartaric Acid*.—Tartarodihydrazide (compare Frankland and Slatore, T., 1903, 83, 1363), obtained from ethyl tartrate and hydrazine hydrate, forms a *dihydrochloride*, a *disalicylidene* derivative, $\text{C}_{18}\text{H}_{18}\text{O}_6\text{N}_4$ a yellowish-white powder, m. p. 261° , a colourless *di-p-anisylidene* derivative, m. p. 231° , a *dipiperonylidene* derivative, pale yellow leaflets, m. p. 216° (decomp.), a *dicinnamylidene* derivative, yellow powder, m. p. 218° , a colourless *di-m-nitrobenzylidene* derivative, m. p. 210° , an *ethyl acetoacetate* derivative, $\text{C}_{16}\text{H}_{28}\text{O}_8\text{N}_4$, colourless, crystalline powder, m. p. 151° , a *diacetyl* derivative, needles, m. p. 216° , and a *dibenzoyl* derivative, light grey crystals, m. p. 219° (decomp.). On treatment with iodine in aqueous alcoholic solution, the dihydrazide undergoes conversion into the cyclic *hydrazide*,

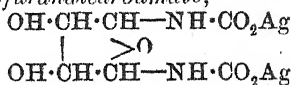
$\text{NH}\cdot\text{CO}\cdot\text{CH}\cdot\text{OH}$
 $\text{NH}\cdot\text{CO}\cdot\text{CH}\cdot\text{OH}$, a yellow powder, which begins to decompose near 220° without melting. The dihydrazide hydrochloride reacts with sodium nitrite solution, producing *tartaric diazide*,

$\text{N}_3\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{N}_3$, colourless crystals, m. p. 66° (decomp.), which is decomposed by aniline or toluidine at 100° with formation of tartaro-dianilide or -ditoluidide and by alcohol or water, giving glyoxal (*m-nitrobenzoyl-osazone*, $\text{C}_{16}\text{H}_{12}\text{O}_6\text{N}_6$, m. p. 320° with decomp.). The addition of phenylhydrazine acetate to a cold aqueous solution of the azide causes the deposition of tartarodiphenylhydrazide.

[With AUGUST DARAPSKY.]—XII. *Hydrazide and Azide of Mucic Acid*.—Ethyl mucate and hydrazine hydrate react in alcoholic solution, forming *mucodihydrazide*,

$\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot[\text{CH}\cdot\text{OH}]_4\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, leaflets, m. p. 215° (decomp.) (*dihydrochloride*, m. p. 204° [decomp.]; *dibenzylidene* derivative, a colourless, amorphous mass, m. p. 221° (decomp.); *disalicylidene* derivative, m. p. 232° (decomp.); *acetone* derivative, $\text{C}_{12}\text{H}_{22}\text{O}_6\text{N}_4$, decomp. near 200°), which is converted by sodium nitrite into *mucic diazide*,

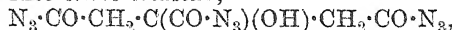
$\text{N}_3\cdot\text{CO}[\text{CH}\cdot\text{OH}]_4\cdot\text{CO}\cdot\text{N}_3$, a microcrystalline powder; the action of aniline on this substance yields mucodianilide, whilst warm alcohol causes the production of free nitrogen, ethyl mucate, carbamic azide, tartardialdehyde, and *dihydroxy-tetrahydrofurandicarbamoyl-γ-dilactone* (annexed formula); the solution of the last-named substance in aqueous sodium hydroxide, on treatment with silver nitrate solution, yields the gelatinous *silver dihydroxytetrahydrofurandicarbamate*,



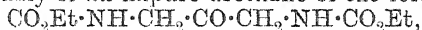
The action of methyl alcohol on mucic diazide is similar to that of ethyl alcohol, whilst water also yields the dilactone, together with tartardialdehyde.

[With FRIEDRICH SAUVIN.]—XIII. *Hydrazide and Azide of Citric Acid*.—Ethyl citrate and hydrazine hydrate in alcoholic solution react, giving *citrotrihydrazide*,

$\text{NH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}(\text{OH})(\text{CO} \cdot \text{NH} \cdot \text{NH}_2) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$, tablets, m. p. 107° (*trihydrochloride*, needles, m. p. 162° ; *tribenzylidene* derivative, colourless crystals, m. p. 227° ; *trisalicylidene* derivative, needles, m. p. 180° (decomp.); *benzophenone* derivative, $\text{C}_{15}\text{H}_{38}\text{O}_4\text{N}_6$, colourless needles, m. p. 159°), which by sodium nitrite is convertible into *citric triazide*,

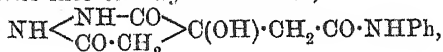


colourless needles, which melt and then explode on warm water. In the presence of much water the triazide decomposes with formation of some azoimide, whilst aqueous ammonia causes the production of citramide, aniline, and *p*-toluidine in ethereal solution, analogously yielding *citro-anilide* and *-p*-toluidide respectively. Warm ethyl alcohol causes decomposition into free nitrogen and a red substance consisting probably of an impure urethane of the formula



whilst dilute hydrochloric acid at 40° gives rise to diaminoacetone. By the interaction of ethyl citrate and hydrazine hydrate in the absence of alcohol there is obtainable *citrohydrazidehydrazide hydrochloride*, $\text{NH} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2 \cdot \text{HCl}$, decomp.

near 200° , which reacts with benzaldehyde, giving the *benzylidene* derivative, $\text{NH} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CHPh}$, a crystalline powder, m. p. near 274° , and with sodium nitrite yielding *citrohydraziazide*, $\text{NH} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{N}_3$; this is a colourless powder which is converted by aniline in the presence of a little alcohol and ether into *citrohydrazianilide*,



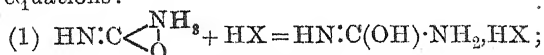
m. p. near 267° (decomp.), and on heating with water gives a yellow, crystalline powder, decomp. near 280° , of uncertain nature.

D. F. T.

The Constitution of Carbamides. IV. The Mechanism of the Interaction of Carbamide [Urea] and Nitrous Acid.

EMIL ALPHONSE WERNER (T., 1917, 111, 863—876).—The reaction between nitrous acid and urea, usually expressed by the equation $\text{CH}_4\text{ON}_2 + 2\text{HNO}_2 = \text{CO}_2 + 2\text{N}_2 + 3\text{H}_2\text{O}$, is commonly regarded as evidence of the carbamide structure, but, without asking why not, chemists have not used the reaction for the estimation of urea, knowing that it is quite valueless for the purpose. The author has now examined the reaction quantitatively, and proves that the above equation is fallacious, being based on a wrong conception of the constitution of urea and not on experimental evidence.

Urea is not attacked by pure nitrous acid, even if a small quantity of a weak acid (for example, acetic acid) is present. Only when a strong acid is present does a reaction take place, that is, the reaction is really that of a salt of urea. It can be demonstrated that one of the initial products is cyanic acid, which is hydrolysed as fast as it is formed, or attacked by more nitrous acid. The actual reactions can therefore be represented by the following equations:



(2) this + $\text{HNO}_2 = \text{N}_2 + \text{HNCO} + 2\text{H}_2\text{O} + \text{HX}$; (3) $\text{HNCO} + \text{H}_2\text{O} = \text{NH}_3 + \text{CO}_2$; (4) $\text{HNCO} + \text{HNO}_2 = \text{CO}_2 + \text{N}_2 + \text{H}_2\text{O}$. Reaction (4) can be almost entirely suppressed in favour of reaction (3) by keeping the concentration of nitrous acid low, and, conversely, if the solutions are concentrated and nitrous acid is in excess, reaction (4) is the predominating one, although it never quite outweighs reaction (3). Only if reaction (4) were quantitatively realised would the proportion of nitrogen to carbon dioxide in the gas conform to the usually accepted equation. The "loss" of nitrogen observed, regarded from the old point of view, is due to the production of ammonia (reaction 3). Another fact which has been overlooked is that nitric oxide is always formed as well, under the ordinary conditions used in the estimation of nitrous acid by urea, even to the extent of 6–8% of the total gas. J. C. W.

Electronic Formula of Benzene and Molecular Volumes of the Chlorobenzenes. HARRY SHIPLEY FRY (*J. Amer. Chem. Soc.*, 1917, **39**, 1688–1699).—Various relationships between the electronic formula of benzene and certain physical properties, notably the molecular volumes, of mono-, di-, tri-, tetra-, penta-, and hexa-chlorobenzenes are indicated and discussed. It is shown that halogen atoms which function positively appear to possess different atomic volumes from those which function negatively, so that it is possible to correlate certain additive and constitutive effects apparent in the molecular volumes of certain compounds with their electronic formulæ; these effects cannot be explained by means of ordinary structural formulæ. Definite relationships which exist between the molecular volumes of six different chlorobenzenes and their respective electronic formulæ lend further support to the electronic formula of benzene. The suggestion is made that any variations in the relative positions of the valency electrons which determine the polarity of an atom may likewise cause variations in the atomic volume of the atom. T. H. P.

Preparation of Benzyl Chloride. J. B. CONANT (U.S. Pat., 1233986, 1917; from *J. Soc. Chem. Ind.*, 1917, **36**, 1002).—A mixture of toluene and bleaching powder or other suitable chlorine compound is treated with sulphur dioxide or other suitable gas reacting with the bleaching powder to form chlorine, and the resulting benzyl chloride separated by distillation. H. W.

Reduction of Nitro- and Nitroso-compounds with Platinum and Hydrogen. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1917, [v], 26, ii, 87—91).—Aromatic mononitro-compounds (*p*-nitrophenol, *p*-nitroanisole, and *p*-nitrotoluene) are reduced to amines by hydrogen and platinum-black at the ordinary temperature, no matter what quantity of hydrogen is present. The aromatic nitroso-compounds behave in the same way (*p*-nitrosophenol, *p*-nitrosothymol, *p*-nitrosodimethylaniline, and the nitrosonaphthols). In the same conditions, terpene nitroso-compounds are reduced quantitatively to the corresponding hydroxylamines; thus, 8-nitrosomenthone is converted into 8-hydroxylaminomenthone.
R. V. S.

Crystallographic Examination of Diphenyl and its Derivatives. KARL MIELEITNER (*Zeitsch. Kryst. Min.*, 1915, 55, 51—87).—The author has examined crystals of about twenty-two ortho- and para-derivatives of diphenyl, but fails to find any certain evidence of morphotropic relationship between a derivative and the parent substance, and few instances of morphotropic relationship among the derivatives.

Diphenyl (m. p. 70°) is monoclinic prismatic [$a:b:c=1.4428:1.54331;\beta=94^{\circ}46'$].

p-p'-Ditolyl is also monoclinic prismatic, but bears no apparent relationship to the parent hydrocarbon [$a:b:c=1.1780:1.07212;\beta=94^{\circ}20'$].

p-p'-Difluoro-, dichloro-, and dibromo-diphenyl form an isomorphous monoclinic series; unfortunately, the di-iodo- and dicyano-compounds could not be completely measured. The axial ratios are as follows:

p-p'-Difluorodiphenyl [$a:b:c=1.1021:1.06954;\beta=96^{\circ}8'$].

p-p'-Dichlorodiphenyl [$a:b:c=1.1504:1.07159;\beta=96^{\circ}53'$].

p-p'-Dibromodiphenyl [$a:b:c=1.1152:1.06942;\beta=96^{\circ}38'$].

Of the other derivatives of the dipara-series, the dihydroxydiphenyl is orthorhombic [$a:b:c=0.8555:1.40194$], whilst dinitrodiphenyl and diaminodiphenyl are triclinic.

The diortho-derivatives, although structurally less symmetrical, frequently crystallise with higher symmetry than the corresponding dipara-compounds. Thus, *o-o'*-dichlorodiphenyl is orthorhombic [$a:b:c=0.8297:1.07459$]; *o-o'*-dihydroxydiphenyl, orthorhombic [$a:b:c=1.1819:1.18277$]; *o-o'*-dinitrodiphenyl, monoclinic [$a:b:c=1.2927:1.09089;\beta=121^{\circ}36\frac{1}{2}'$]; *o-o'*-diaminodiphenyl, monoclinic [$a:b:c=1.3522:1.33760;\beta=100^{\circ}19\frac{1}{2}'$].

The crystals of other mono- and di-derivatives of diphenyl are described, and also those of di-diphenylmethane. It is concluded that the magnitude of the change of crystal structure effected by any substituent group bears no relation to the size of that group. The topic parameters appear to throw no fresh light on the morphotropic relationships.
E. H. R.

Pyro-condensations in the Aromatic Series. II. HANS MEYER and ALICE HOFMANN (*Monatsh.*, 1917, 38, 141—157. Compare *ibid.*, 1917, 37, 681).—Aromatic derivatives of the four

halogens have been maintained for some hours at a bright red heat and the products examined. In all cases, halogen and hydrogen are eliminated together; it is never found, except perhaps to a doubtful extent in the case of iodine, that two aromatic nuclei are united by the carbon atoms which bore the halogen atoms.

Chlorobenzene yields 4:4'-dichlorodiphenyl and some *p*-chlorodiphenyl and 2:2'-dichlorodiphenyl, hydrogen chloride and a trace of chlorine being evolved. *p*-Dichlorobenzene is particularly stable, but gives after a time 2:5:2':5'-tetrachlorodiphenyl, yellow crystals, m. p. 84—85°.

The decomposition of bromobenzene is greatly helped by mercury vapour. The products are benzene and *p*-bromodiphenyl, m. p. 87—88°. *p*-Dibromobenzene yields 4:4'-dibromodiphenyl, m. p. 162—163°; 2:4'- or 2:2'-dibromodiphenyl, m. p. 117°, a very little bromobenzene, and sometimes 2:5:2':5'-tetrabromodiphenyl, m. p. 210—211°.

Iodobenzene yields benzene, some diphenyl, and a mixture of iododiphenyls.

Fluorobenzene forms 4:4'-difluorodiphenyl, m. p. 94—95°.

o-Bromotoluene most readily yields anthracene and probably 2:2'-dibromostilbene and 2:2'-dibromodiphenyl. *p*-Chlorotoluene gives 4:4'-dichlorodibenzyl and 4:4'-dichlorostilbene. *p*-Fluorotoluene decomposes quickly and at not a very high temperature, but the only important product is 4:4'-difluorostilbene, $C_{14}H_{10}F_2$, m. p. 106°. This slowly combines with bromine to form 4:4'-difluoro-*aa'*-dibromodibenzyl, in compact needles, m. p. 141—142°. *m*-Fluorotoluene yields chiefly 3:3'-difluorodibenzyl, which crystallises in broad lamellæ, m. p. 38°. *p*-Iodotoluene forms some toluene, dibenzyl, stilbene, and 4:4'-di-iodostilbene, colourless leaflets, m. p. 257—259°.

Benzyl chloride yields stilbene, toluene, and a trace of dibenzyl, but no phenanthrene. J. C. W.

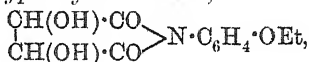
Tetraphenylmethane. M. GOMBERG and OLIVER KAMM (*J. Amer. Chem. Soc.*, 1917, **39**, 2009—2015).—A report of attempts to improve the yield of tetraphenylmethane obtainable by various methods. The action of magnesium phenyl bromide on chlorotriphenylmethane gives only a poor yield of tetraphenylmethane, the product being largely triphenylmethyl; this result is not due to the subsequent decomposition of tetraphenylmethane by the Grignard reagent or to a primary formation of triphenylmethyl followed by a slow reaction of this with the Grignard reagent producing tetraphenylmethane. It is found, however, that when the action is effected in the absence of ether and at 150—200°, 10—12% of the tetraphenyl compound can be obtained instead of the usual 3—5%, and the product is not contaminated with triphenylmethyl peroxide as is the ordinary product at lower temperatures.

The methyl and ethyl ethers of triphenylcarbinol react with magnesium phenyl bromide at 150—160°, giving 10—12% of tetraphenylmethane, whilst with the phenyl ether the yield is 20%.

Triphenylcarbinol and chlorotriphenylmethane readily condense with phenol at 100° in the presence of a small quantity of an acid, such as sulphuric or hydrochloric, forming *p*-hydroxytetraphenylmethane in almost quantitative amount; if sodium phenoxide is used and the presence of acid is avoided, the product is phenoxytriphenylmethane, the occasional simultaneous presence of hydroxytetraphenylmethane in the product being probably due to an intermediate formation of triphenylmethyl, which subsequently reacts additively with the free phenol present. From the readiness with which *p*-hydroxytetraphenylmethane is produced, it is evident that the hindrance to the formation of tetraphenylmethane is not of a simple steric nature.

D. F. T.

Amides and Imides of Tartaric Acid. III. L. CASALE (*Gazzetta*, 1917, 47, ii, 63—68. Compare this vol., i, 545).—When *p*-phenetidine hydrogen tartrate is kept at 150—155° for some hours, *p*-ethoxyphenyltartramide,



is formed (yield, 65%). The imide is insoluble in cold water and is not saponified when boiled with water for a long time; it has m. p. 260° (corr.), $[\alpha]_D^{25} + 115.7^\circ$. When this imide is heated at 150—160° with an equal weight of *p*-phenetidine, *diethoxyphenyltartramide*, $\text{C}_{20}\text{H}_{24}\text{O}_6\text{N}_2$, m. p. 282° (corr.), is formed. *Ethoxyphenyltartramide*, $\text{C}_{12}\text{H}_{16}\text{O}_5\text{N}_2$, is produced when the above-mentioned imide is dissolved in warm concentrated aqueous ammonia; it crystallises in colourless, prismatic tablets, m. p. 237° (corr.; decomp.). *Ethoxyphenyltartramic acid*, $\text{C}_{12}\text{H}_{15}\text{O}_6\text{N}$, is obtained by boiling the imide with a 2*N*-solution of potassium hydroxide and acidifying the solution with concentrated hydrochloric acid. It crystallises in leaflets, m. p. 201° (corr.), and has $[\alpha]_D^{25} + 107.1^\circ$. Its *methyl* ester, $\text{C}_{13}\text{H}_{17}\text{O}_6\text{N}$, forms shining prisms, m. p. 191° (corr.), $[\alpha]_D^{25} + 101.2^\circ$. The *ethyl* ester, $\text{C}_{14}\text{H}_{19}\text{O}_6\text{N}$, crystallises in colourless prisms, m. p. 175° (corr.), and has $[\alpha]_D^{25} + 98.72^\circ$.

R. V. S.

Steric Hindrance of Chemical Reactions. III. *ψ*-Cumylsulphamic Acid [*ψ*-Cumylaminosulphonic Acid]. C. PAAL and MAX HUBALECK (*Ber.*, 1917, 50, 1110—1115. Compare A., 1899, i, 587, 748; 1901, i, 693).—*ψ*-Cumidine reacts with aminosulphonic acid at moderate temperatures to form *ψ*-cumidine aminosulphonate, $\text{NH}_2\text{·SO}_3\text{H·NH}_2\text{·C}_6\text{H}_2\text{Me}_3$, in stout, elongated, glistening leaflets, m. p. 163°, which changes at 165—170° into ammonium *ψ*-cumylaminosulphonate, $\text{C}_6\text{H}_2\text{Me}_3\text{·NH·SO}_3\text{·NH}_4$. When a mixture of *ψ*-cumidine and aminosulphonic acid is heated at 170—180°, however, the product is *ψ*-cumidine *ψ*-cumylaminosulphonate, which crystallises in concentric groups of sparingly soluble, glistening needles, m. p. 213°. This can be converted into the corresponding barium and sodium ($1\text{H}_2\text{O}$) salts, and from the latter the free *ψ*-cumylaminosulphonic acid (2:4:5-trimethyl-

phenylaminosulphonic acid) can be isolated in satiny needles, decomp. 225° .

It was found to be impossible to obtain either of the two possible ψ -cumidinesulphonic acids, by heating these ψ -cumylaminosulphonates, or by the action of fuming sulphuric acid on ψ -cumidine. J. C. W.

ψ -Cumylnitrosoaminosulphonic Acid. C. PAAL and MAX HUBALECK (*Ber.*, 1917, **50**, 1115—1118).—A suspension of ψ -cumylaminosulphonic acid in water, when treated with sodium nitrite in the cold, gives a crystalline mass of the sodium salt of the nitroso-acid, from which the free acid can be isolated by the careful addition of dilute hydrochloric acid at a low temperature. *ψ -Cumylnitrosoaminosulphonic acid* (2 : 4 : 5-trimethylphenylnitrosoaminosulphonic acid), $C_6H_2Me_3N(NO)SO_3H$, crystallises in white needles, and greatly resembles diazonium salts. It explodes on warming, and even spontaneously when dry, and may also explode when warmed with dilute acids. With slightly acidified water, it decomposes into nitrogen and ψ -cumenol, and when warmed with alcohol it yields ψ -cumene. J. C. W.

The Three Nitrotriphenylamines. JEAN PICCARD and LOUIS M. LARSEN (*J. Amer. Chem. Soc.*, 1917, **39**, 2006—2009).—By heating with iodobenzene, potassium carbonate, copper powder, and a little potassium iodide, a nitrobenzene solution of *p*-nitrodiphenylamine was made to yield the corresponding *p*-nitrotriphenylamine, m. p. 140° , identical with the product obtainable by direct nitration of triphenylamine (Herz, A., 1890, 1409). In a similar manner, *o*- and *m*-nitrodiphenylamines respectively were converted into the previously unknown *o*-nitrotriphenylamine, $C_{18}H_{14}O_2N_2$, orange-yellow crystals, m. p. 98° , and *m*-nitrotriphenylamine, a lemon-yellow solid, m. p. 78° , the solution of which in sulphuric acid acquires a blue coloration in a few seconds.

D. F. T.

The Bromination of the Two Naphthylamines. HARTWIG FRANZEN and ERLING AASLUND (*J. pr. Chem.*, 1917, [ii], **95**, 160—167. Compare Franzen and Eidis, A., 1914, i, 162; Franzen and Henglein, A., 1915, i, 230).—It has already been shown that the naphthylamines, by conversion into their benzylidene derivatives, addition of bromine, and subsequent decomposition of the additive compounds, can be made to yield bromo-substituted naphthylamines. Further experiments are now described, as a result of which it is possible to state that only two atoms of bromine can with ease be introduced into α -naphthylamine, whilst the introduction of three is possible with β -naphthylamine.

1 : 2-Dibromo- β -naphthylamine, which has already been prepared in the above way, forms a *benzylidene* derivative, $C_{12}H_{11}NBr_2$, yellow needles, m. p. 101 — 103° ; the dark grey dibromide, $C_{12}H_{11}NBr_4$, of this substance when boiled with alcohol regenerates the dibromonaphthylamine.

1-Bromobenzylidene- β -naphthylamine when successively treated in chloroform solution with bromine, pyridine, bromine, and boiling alcohol is converted into 1:6:7-tribromo- β -naphthylamine (compare Claus and Philipson, A., 1891, 462), which, like 2:4:6-tribromoaniline, does not form a benzylidene derivative. In an attempt to prepare a tetrabromo-derivative of β -naphthylamine, benzylidene-naphthylamine was thrice treated with bromine and pyridine successively, and then finally with bromine and alcohol successively, but the product was only the 1:6:7-tribromo- β -naphthylamine.

Benzylidene- α -naphthylamine is, by this method, readily convertible into 2:4-dibromo- α -naphthylamine, which, however, resisted the endeavour at further bromination by this process, the product obtained by decomposition of the dibromide of the benzylidene derivative being impure 2:4-dibromo- α -naphthylamine, the same substance being formed from benzylidene- α -naphthylamine after two successive treatments with bromine and pyridine and a final treatment with bromine and alcohol. D. F. T.

Preparation of Phenyl- α -naphthylamine. M. KATAYAMA (*Kogyo-Kwagaku-Zasshi*; [*J. Chem. Ind., Tokyo*], 1917, 20, 353—365; from *J. Soc. Chem. Ind.*, 1917, 36, 865).—Streff's method of preparing phenyl- α -naphthylamine by combination of α -naphthylamine hydrochloride and aniline is tedious and gives a relatively poor yield. The author made experiments to ascertain the most suitable conditions for preparing the base by Friedländer's method of condensing aniline with α -naphthol in presence of a dehydrating agent. Under the following conditions, a yield of 64% of the theoretical quantity of phenyl- α -naphthylamine (calculated on the α -naphthol used) is obtained. An intimate mixture of α -naphthol (1 mol.), aniline (2 mols.), and calcium chloride (1 mol.) is placed in an autoclave, which is heated for ten hours at 300°. The product is treated with boiling water to remove calcium chloride, with hydrochloric acid to remove uncombined aniline, and with sodium hydroxide to remove uncombined α -naphthol, and is then distilled in a vacuum in a current of carbon dioxide or hydrogen. After crystallising from alcohol, the phenyl- α -naphthylamine has m. p. 60°. T. S. P.

The Influence of the Solvent on the Reaction between Polyhydric Phenols and Alkali Hydrogen Carbonates. FRANZ VON HEMMELMAYR (*Monatsh.*, 1917, 38, 77—89. Compare A., 1913, i, 468; 1915, i, 543).—The reaction between potassium hydrogen carbonate and polyhydric phenols under different conditions has been studied.

A. *Anhydrous Agents; Atmospheric Pressure.*—Resorcinol, at 120°, yields 2:4- and 2:6-dihydroxybenzoic acids; catechol and quinol produce no carboxylic acids. Pyrogallol yields 2:3:4-trihydroxybenzoic acid.

B. *Anhydrous Agents; Closed Tubes.*—Catechol at 200° yields catecholdicarboxylic acid; resorcinol forms α -resodicarboxylic acid, and 3:5-dihydroxybenzoic acid yields β -resodicarboxylic acid; quinol

at 260—270° gives a high yield of a dicarboxylic acid, which crystallises in needles with $1\text{H}_2\text{O}$; pyrogallol at 200° forms gallo-carboxylic acid, m. p. 281°, the yield being almost the theoretical one; orcinol gives *p*-orsellinic acid. 1:5-Dihydroxynaphthalene at 230° yields a *dicarboxylic acid*, which decomposes at 290° and then melts at 300°; the acid and its alkali salts dye wool yellow, and the shade is converted into a very good brown by treatment with chromic acid or chromates. The *barium*, *calcium*, *silver*, and *ammonium* salts are described. 1:6-Dihydroxynaphthalene reacts with a mixture of the hydrogen carbonate and normal carbonate to form a *monocarboxylic acid*, in stellate groups of yellow prisms, m. p. 200°; the *barium* salt crystallises with $8\text{H}_2\text{O}$. Other dihydroxynaphthalenes were examined, but no acids could be obtained.

C. *Reactions in the Presence of Dry Aniline or Diphenylamine; Atmospheric Pressure.*—Resorcinol yields β -resorcylic acid and also α -resodicarboxylic acid, especially with diphenylamine, although this acid loses carbon dioxide most readily if heated alone with the bases. Catechol and quinol do not react, and pyrogallol forms only a monocarboxylic acid.

D. *Reactions in Boiling Anhydrous Cetyl Alcohol.*—Although this alcohol boils at a higher temperature than diphenylamine, the yield of α -resodicarboxylic acid from resorcinol is not so great as in the above case.

J. C. W.

Compounds of Ferric Chloride with Ethyl Ether and with Benzyl Sulphide. AQUILA FORSTER, CHRISTOPHER COOPER, and GEORGE YARROW (T., 1917, 111, 809—814).—Anhydrous ferric chloride dissolves in ethyl ether to form the dark red, very deliquescent compound, $\text{C}_4\text{H}_{10}\text{O} \cdot \text{FeCl}_3$. This gives a quantitative yield of ethyl chloride when heated over a free flame, and reacts with ammonia to form products which evolve ethylamines on distillation.

A double compound of benzyl sulphide and ferric chloride, $\text{S}(\text{C}_7\text{H}_7)_2 \cdot \text{FeCl}_3$, has also been obtained, in minute, lemon-yellow crystals, m. p. 94°. This reacts with benzyl chloride to form tribenzylsulphinium ferrichloride, m. p. 98.5° (Hofmann and Ott, A., 1907, i, 84), which can be converted into the impure, viscous chloride by means of alkali. A compound, $\text{S}(\text{C}_7\text{H}_7)_3 \cdot \text{CN} \cdot \text{FeCl}_3$, lemon-yellow crystals, m. p. 76°, is obtained by the interaction of benzyl sulphide, benzyl cyanide, and ferric chloride in ethereal solution. Ammonia converts this into *tribenzylsulphinium cyanide*, $\text{S}(\text{C}_7\text{H}_7)_3 \cdot \text{CN}$, large, white prisms, m. p. 41°, which combines with platinum chloride, as well as with ferric chloride, giving a red compound, $\text{C}_{44}\text{H}_{42}\text{N}_2\text{S}_2 \cdot \text{PtCl}_4$, m. p. 162°.

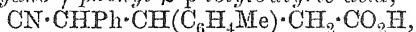
J. C. W.

***p*-Dimethylaminobenzoyl Chloride.** H. STAUDINGER and R. ENDLE (Ber., 1917, 50, 1046—1047).—*p*-Dimethylaminobenzoyl chloride may be obtained in white leaflets, m. p. 145—147°, by the action of thionyl chloride on the corresponding acid, and converted into *p*-dimethylaminobenzanilide, m. p. 182—183°. Just as the reactivity of the carbonyl group in benzaldehyde or benzophenone

is greatly enhanced by the presence of a methoxyl or dimethyl-amino-group in the para-position, so *p*-methoxy- and especially *p*-dimethylamino-benzoyl chlorides are found to be more chemically active than benzoyl chloride.

J. C. W.

Action of Sodium Benzyl Cyanide with Ethyl *p*-Tolylcinnamate. MILO REASON DAUGHTERS (*J. Amer. Chem. Soc.*, 1917, **39**, 1927—1930).—The interaction of ethyl *p*-tolylcinnamate, benzyl cyanide, and sodium methoxide did not follow the expected course, but yielded γ -cyano- γ -phenyl- β -*p*-tolylbutyric acid,



m. p. 166—169°, together with a substance which, from analogy with the results of Avery and McDole (*A.*, 1908, i, 343), may have the constitution $\text{CN}\cdot\text{CPh}\left\langle\begin{array}{l}\text{CH}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}_2\cdot\text{CO} \\ \text{CH}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}_2\cdot\text{CO}\end{array}\right\rangle\text{O}$.

D. F. T.

Method of Separation of Stereoisomeric α -Halogenated Ethylenic Acids (Stable and Labile). J. BOUGAULT (*Bull. Soc. chim.*, 1917, [iv], **21**, 172—174).—The method used for the separation of the stereoisomeric α -iodocinnamic acids (compare *A.*, 1916, i, 817) is shown to be generally applicable to α -halogenated ethylenic acids, and more detailed instructions are given.

W. G.

β -Alkylated Cinnamic Acids and their Stereoisomerides. R. STOERMER, F. GRIMM, and E. LAAGE (*Ber.*, 1917, **50**, 959—980).—A number of β -alkylcinnamic acids and their esters, amides, and anilides are described, of both stable and *allo*-forms. Each pair of acids is remarkable among stereoisomeric acids in giving solid solutions of the two forms, which often appear to be composed of one kind of crystal, and are extremely difficult to separate. Furthermore, it frequently happens that the *allo*-acid has a higher m. p. than the stable acid, although the usual rule is observed in all but the case of the β -ethylcinnamic acids, namely, that the isomeride with the lower m. p. has by far the greater solubility. Consequently, it is often difficult to determine in those cases in which both forms are produced during the same synthesis which is the stable and which the *allo*-modification. The amides and anilides show similarly irregular physical properties, but the methyl esters regularly have lower boiling points in the *allo*-series and the *allo*-acids can be converted into indones (this vol., i, 654). The acids may usually be separated by means of light petroleum, but, owing to the prevailing scarcity of this solvent, other methods have been investigated. It is found that the basic copper salts of the *allo*-ethyl- and -propyl acids are much less soluble in ether than the isomerides, but the acids are all so weak that they do not yield aniline salts, and a separation by means of these is therefore impossible. The mixtures of isomerides are all much more soluble than either ingredient.

The labile acids may all be prepared by exposing the stable acids to the light of a quartz mercury lamp, and the methyl esters are obtained by means of methyl sulphate, in order to avoid any agents which favour transformation of the *allo*-form.

Stable β -methylcinnamic acid is best obtained by the action of

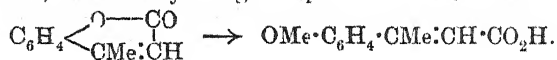
zinc filings and ethyl bromoacetate on acetophenone, a few drops of phosphoryl chloride being added before the distillation to ensure the complete decomposition of the β -hydroxy-acid which is first formed. The acid crystallises in rhombic prisms, m. p. 98.5° , and dissolves in sulphuric acid with lemon-yellow colour; the methyl ester forms large, stout crystals, m. p. 29° , b. p. $127-128^\circ/10$ mm.; the *amide* crystallises in stout needles, m. p. 119° ; the anilide forms slender needles, m. p. 121° (compare Henrich and Wirth, A., 1904, i, 431). *allo- β -Methylcinnamic acid* crystallises in very thin, flat rhombs, m. p. 131.5° ; the *methyl* ester has m. p. $26.5-27.5^\circ$, b. p. $113.5^\circ/8$ mm.; the *amide* forms iridescent leaflets, m. p. $94-95^\circ$; the *anilide* separates as a woolly mass, m. p. 93° .

β -Ethylcinnamic acid, obtained in a similar manner from propiophenone, crystallises in very large, elongated platelets, m. p. 95.5° ; the *methyl* ester has b. p. $130^\circ/8$ mm.; the *amide* forms asbestos-like needles, m. p. 104° ; the *anilide* has m. p. 84° . *allo- β -Ethylcinnamic acid* crystallises in stout rhombs, m. p. $93-95.5^\circ$; the *methyl* ester has b. p. $122-123^\circ/8$ mm.; the *amide* forms iridescent leaflets, m. p. 101° ; the *anilide* has m. p. 122° .

β -Propylcinnamic acid, likewise obtained by Schroeter's method (A., 1907, i, 530), has m. p. 94° , and the *amide* forms woolly needles, m. p. 98.5° . *allo- β -n-Propylcinnamic acid* crystallises in long, stout needles, m. p. 86.5° , and the *amide* forms glistening leaflets, m. p. $100-101^\circ$. A mixture of the two acids forms homogeneous crystals, m. p. $59-60^\circ$.

p- β -Dimethylcinnamic acid (*ibid.*) crystallises in stout fibres, m. p. 135° ; the *methyl* ester forms thin leaflets, m. p. $45-45.5^\circ$, b. p. $157^\circ/17$ mm.; the *amide* has m. p. $131-132^\circ$. *allo-p- β -Dimethylcinnamic acid* crystallises in brilliant leaflets, m. p. $117.5-118^\circ$; its *methyl* ester has b. p. $144-145^\circ/17$ mm.; the *amide* forms long needles, m. p. 106° .

o-Methoxy- β -methylcinnamic acid may be prepared from *o*-methoxyacetophenone and methyl bromoacetate, whereby precautions are necessary to avoid obtaining a mixture with the *allo*-modification. The stable acid forms feathery tablets, m. p. 96.5° , and the *methyl* ester has b. p. $172-173^\circ/26$ mm. *allo-o-Methoxy- β -methylcinnamic acid* may be obtained by the action of ultra-violet light on the stable acid or by hydrolysing 4-methylcoumarin (A., 1908, i, 339) and methylating the phenolic acid, thus:



It has m. p. $123-124^\circ$, and its *methyl* ester has b. p. $157.5-158.5^\circ/25$ mm.

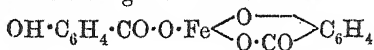
p-Methylcinnamic acid crystallises in large scales, m. p. $198-199^\circ$; its *methyl* ester has m. p. $57-58^\circ$, b. p. $164-165^\circ/32$ mm.; its *amide* forms white leaflets, m. p. $189-190^\circ$. *allo-p-Methylcinnamic acid* crystallises in bundles of stout needles, m. p. $75-76^\circ$, and forms an *aniline hydrogen* salt, woolly needles, m. p. $86-87^\circ$, a *methyl* ester, b. p. $141-142^\circ/23$ mm., and an *amide*, m. p. $116-116.5^\circ$.

J. C. W.

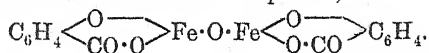
The Optical Isomerism of the Abietic Acids. FERD. SCHULZ (*Chem. Zeit.*, 1917, **41**, 666—667).—Abietic acid may be prepared by extracting American colophony with dilute alcohol or by precipitating the alcoholic solution with hydrogen chloride, but the author finds that whereas the alcoholic solution of the resin has +rotation, the solution becomes levorotatory on addition of hydrogen chloride, so that the products above mentioned are probably not identical. When the resin is dissolved in boiling alcohol and dry hydrogen chloride passed into the cold solution, white crystals of abietic acid are obtained, the constants of which gradually alter on recrystallisation from acetone, from $[\alpha]_D -77.9^\circ$ (solvent and concentration not stated) and m. p. 161° to $[\alpha]_D -96.8^\circ$, m. p. 171° . Further recrystallisation from acetone raises the m. p. to 173° . The molecular weight by titration is found to be 304. On exposure to air, the rotation alters owing to oxidation, and it changes also on heating at high temperatures (200°). American colophony, type H, extracted with dilute alcohol, yields an oil which gradually sets to a mass of crystals, from which by crystallisation from acetone a portion is obtained having $[\alpha]_D -22^\circ$ ($c=2.2$; solvent not stated), whilst another part has $[\alpha]_D +49^\circ$. An almost inactive fraction, $[\alpha]_D +2.6^\circ$, is also obtained. On treatment with mineral acid, the rotation of the two last became negative.

From technical resin oil the author has extracted an acid which he names *ölsylvic acid* (Ölsylvinsäure), m. p. $171-173^\circ$, $[\alpha]_D +53^\circ$ ($c=10$; solvent not stated), which does not alter in rotation when warmed with mineral acids, and in contradistinction to the abietic acid from colophony does not absorb oxygen from the air and does not turn yellow in light. The abietic acids can readily be esterified by boiling their alcoholic solutions with 30% of concentrated sulphuric acid for an hour. T. S. PA.

Iron Compounds of Salicylic Acid. R. F. WEINLAND and KURT ZIMMERMANN (*Arch. Pharm.*, 1917, **255**, 204—232).—The paper is largely a reply to Claasz's criticisms (*Arch. Pharm.*, 1915, **253**, 342) of Weinland and Herz's classification of the ferric compounds of salicylic acid into three groups (A., 1913, i, 1189). The substance to which Claasz gives the formula



is shown to contain varying amounts of bivalent iron and to be a mixture of salicylic acid compounds of bi- and ter-valent iron. The same is also true of Claasz's compound,



Weinland and Herz's hexasalicylatotri ferric salicylate (*loc. cit.*) cannot have the constitution given to it by Claasz. By treating an alcoholic solution of the substance with *N*-nitric acid, 20% perchloric acid solution, and concentrated sulphuric acid respectively, salts of the following composition have been obtained:

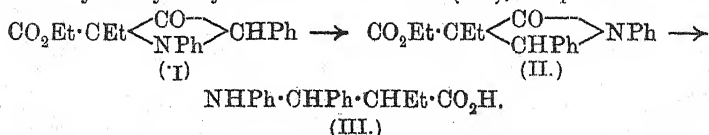
- (i) $\left[\text{Fe}_3 \begin{array}{c} (\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_6 \\ \text{OH} \end{array} \right] \text{NO}_3 \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH} +$
 $\left[\text{Fe}_3 \begin{array}{c} (\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_6 \\ \text{OH} \end{array} \right] (\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_2 + 15 \text{ or } 4\text{H}_2\text{O},$
 brownish-red rectangular plates, (ii) $\left[\text{Fe}_3 \begin{array}{c} (\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_6 \\ (\text{OH})_2 \end{array} \right] \text{ClO}_4 +$
 $\left[\text{Fe}_3 \begin{array}{c} (\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_6 \\ (\text{OH})_2 \end{array} \right] \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} + 4\text{H}_2\text{O},$
 brownish-yellow, crystalline powder, and
 (iii) $\left[\text{Fe}_3 \begin{array}{c} (\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_6 \\ (\text{OH})_2 \end{array} \right] (\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}) +$
 $\left[\text{Fe}_2 \begin{array}{c} (\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_6 \\ (\text{OH})_2 \end{array} \right] \text{SO}_4 +$
 $\left[\text{Fe}_3 \begin{array}{c} (\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_6 \\ (\text{OH})_3 \end{array} \right] (\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}) + 8\text{H}_2\text{O},$
 yellowish-red, crystalline powder. C. S.

Metallic Salts of Acetylsalicylic [*o*-Acetoxybenzoic] Acid. M. BOUVER (*Bull. Sci. Pharmacol.*, 1917, **24**, 86—90; from *Chem. Zentr.*, 1917, ii, 101—102).—The author describes the preparation of aspirin and its known mineral salts. *Magnesium o-acetoxybenzoate* is obtained by treating aspirin with calcined magnesium and water; the precipitate is extracted with methyl alcohol, and the solution precipitated with ether. The salt crystallises in hexagonal plates with 3 or 4H₂O, which are soluble in water or methyl alcohol, but slightly so in ethyl alcohol. A bibliography of other salts is given. H. W.

Ketens. XXVIII. Ketencarboxylic Esters and Schiff's Bases. H. STAUDINGER (*Ber.*, 1917, **50**, 1035—1041).—The author has previously found that coloured ketoketens react with Schiff's bases, but he believed that colourless ketens were less reactive. He now reports that no such connexion between colour and additive capacity exists.

[With R. ENDLE.]—Benzylideneaniline reacts with ordinary keten at 180—200° to form the *lactam* of *β-anilino-β-phenylpropionic acid*, $\text{NPh} \begin{array}{c} \text{CHPh} \\ \text{CO} \end{array} \text{CH}_2$, which crystallises in long leaflets, m. p. 153—154°, and decomposes at 600° into phenylcarbimide and styrene.

[With J. MODRZEJEWSKI.]—Ethyl ketencarboxylate and benzylideneaniline unite at −20° to form *ethyl 3-keto-1:2-diphenyl-4-ethyltrimethylenimine-4-carboxylate* (I), m. p. about 66°. This is very unstable, and changes at 200° into the *lactam* of *α-carbethoxy-β-anilino-β-phenyl-α-ethylpropionic acid* (II), m. p. 109—110°, which may be hydrolysed to the free acid (III), m. p. 154—155°.

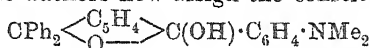


[With H. HIRZEL.]—Methyl phenylketencarboxylate reacts with benzyldeneaniline to yield the lactam of α -carbomethoxy- β -anilino- $\alpha\beta$ -diphenylpropionic acid, $\text{CO}_2\text{Me}\cdot\text{CPh}\langle\text{CO}\rangle\text{NPh}$, m. p. 158—159°, and with diphenylmethyleneaniline (benzophenoneanil) to form methyl 4:6-diketo-1:2:2:3:5-pentaphenylpiperidine-3:5-dicarboxylate, m. p. 213—214° (decomp.).

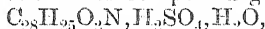
Ethyl ketendicarboxylate does not react with benzyldeneaniline, but with benzophenoneanil it forms a trimethyleneimine derivative.

J. C. W.

Certain Derivatives of *p*-Dialkylamino-*o*-benzoylbenzoic Acids. J. PÉRARD (*Ann. Chim.*, 1917, [ix], 7, 340—414; 8, 22—69).—In part a more detailed account of work already published (compare A., 1906, i, 755; 1908, i, 422). As a result of further work, the authors now assign the constitution

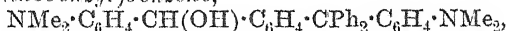


to the compound, m. p. 194°, obtained by the action of excess of magnesium phenyl bromide on the isomeric methyl *p*-dimethylamino-*o*-benzoylbenzoates. This compound gives a sulphate,



m. p. 140—150°; a hydrochloride, $\text{C}_{28}\text{H}_{25}\text{O}_2\text{N}, \text{HCl}, \text{H}_2\text{O}$, m. p. 140—150°; and a platinichloride, m. p. 190—200°. With hydroxylamine it gives a compound, $\text{C}_{28}\text{H}_{26}\text{O}_3\text{N}_2$, m. p. 179° (decomp.). The dimethylaminodiphenylanthracene obtained by the action of concentrated sulphuric acid on *p*-dimethylamino-*o*-benzhydriyltriphenylcarbinol, when reduced by sodium amalgam in methyl-alcoholic solution, gives 10-phenyl-9-*p*-dimethylaminophenyl-9:10-dihydroanthracene, $\text{CHPh}\langle\text{C}_6\text{H}_4\rangle\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, m. p. 184°.

p-Dimethylamino-*o*-benzhydriyltriphenylcarbinol condenses with dimethylaniline, yielding *p*-dimethylaminobenzhydriyl(diphenyl-*p*-dimethylaminobenzyl)benzene,



m. p. 122°, and with diethylaniline, giving *p*-dimethylaminobenzhydriyl(diphenyl-*p*-diethylaminobenzyl)benzene, m. p. 128°. 1-Hydroxy-2:2-diphenyl-1-*p*-dimethylaminophenyl-1:2-dihydroisobenzofuran also condenses with dimethyl- and diethyl-aniline. With the former it gives 2:2-diphenyl-1:1-di-*p*-dimethylaminophenyl-1:2-dihydroisobenzofuran, $\text{CPh}_2\langle\text{C}_6\text{H}_4\rangle\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$,

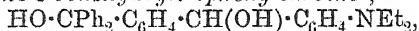
occurring into two crystalline forms: (1) prisms, m. p. 160°; (2) long needles, m. p. 166°. This compound when reduced with zinc and acetic acid yields *o*-phenylbenzyl-di-(*p*-dimethylamino)triphenylmethane, $\text{CHPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, m. p. 225°. With diethylaniline, the product of condensation is 2:2-diphenyl-1-*p*-dimethylaminophenyl-1-*p*-diethylaminophenyl-1:2-dihydroisobenzofuran, m. p. 150°. These condensation products when heated with concentrated sulphuric acid yield the following anthracene deriv-

atives: 10-hydroxy-10-phenyl-9:9-di(-p-dimethylaminophenyl)-9:10-dihydroanthracene, $\text{HO} \cdot \text{CPh} \left\langle \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \right\rangle \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, m. p. 228°, which with dimethylaniline yields 10-phenyl-9:9:10-tri(-p-dimethylaminophenyl)-9:10-dihydroanthracene, m. p. 264°, with diethylaniline, the corresponding 10-phenyl-9:9-di(-p-dimethylaminophenyl)-10-p-diethylaminophenyl-9:10-dihydroanthracene, m. p. 260°, with hydrochloric acid in methyl alcohol the 10-methyl ether, m. p. 175°, and in ethyl alcohol the 10-ethyl ether, m. p. 170°, and on reduction with zinc and acetic acid, 10-phenyl-9:9-di(-p-dimethylaminophenyl)-9:10-dihydroanthracene, m. p. 283°. The condensation product, m. p. 150°, from diethylaniline with concentrated sulphuric acid yields 10-hydroxy-10-phenyl-9-p-dimethylaminophenyl-9-diethylaminophenyl-9:10-dihydroanthracene, m. p. 214°.

A similar series of reactions has been carried out starting with methyl *p*-diethylamino-*o*-benzoylbenzoate, and the following compounds have been prepared:

1-Hydroxy-1-*p*-diethylamino-2:2-diphenyl-1:2-dihydroisobenzofuran, m. p. 160°, giving a methyl ether, m. p. 138–139°, an ethyl ether, m. p. 118°, and with hydroxylamine a compound, $\text{C}_{30}\text{H}_{30}\text{O}_2\text{N}_2$, m. p. 205°.

p-Diethylamino-*o*-benzhydrioltriphenylcarbinol,



m. p. 140°.

2:2-Diphenyl-1:1-di(-*p*-diethylaminophenyl)-1:2-dihydroisobenzofuran, m. p. 163°.

2:2-Diphenyl-1-*p*-diethylaminophenyl-1-*p*-dimethylaminophenyl-1:2-dihydroisobenzofuran, m. p. 150°.

10-Hydroxy-10-phenyl-9:9-di(-*p*-diethylaminophenyl)-9:10-dihydroanthracene, $\text{HO} \cdot \text{CPh} \left\langle \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \right\rangle \text{C}(\text{C}_6\text{H}_4 \cdot \text{NEt}_2)_2$, m. p. 225°.

10-Phenyl-9:9-di(-*p*-diethylaminophenyl)-10-*p*-diethylaminophenyl-9:10-dihydroanthracene, m. p. 258°.

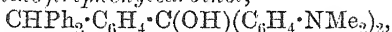
10-Phenyl-10-*p*-dimethylaminophenyl-9:9-di(-*p*-diethylaminophenyl)-9:10-dihydroanthracene, m. p. 220°.

That the above anthracene derivatives have the constitution assigned to them was shown by the fact that tetramethyldiaminodiphenylanthrone when acted on with magnesium phenyl bromide yielded 10-hydroxy-10-phenyl-9:9-di(-*p*-dimethylaminophenyl)-9:10-dihydroanthracene, agreeing in its chemical and physical properties with the same compound described above.

When methyl *p*-dimethylamino-*o*-benzylbenzoate is acted on with magnesium phenyl bromide, it yields *p*-dimethylaminobenzyltriphenylcarbinol, $\text{HO} \cdot \text{CPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, m. p. 139°, and *p*-dimethylaminobenzylbenzopinacone,

$\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}(\text{OH}) \cdot \text{CPh}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, m. p. 210° (decomp.). The carbinol when heated with sulphuric acid yields the compound, $\text{C}_{28}\text{H}_{26}\text{ON} \cdot \text{SO}_3\text{H}$, m. p. 240° (decomp.). With hydrogen chloride in benzene solution it yields the compound, $\text{C}_{28}\text{H}_{26}\text{NCl}$, m. p. 149°, and it gives a platinumchloride, m. p.

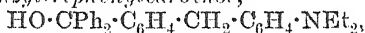
180° (decomp.). When oxidised with chloroanil, the carbinol gives 1-hydroxy-2 : 2-diphenyl-1-*p*-dimethylaminophenyl-1 : 2-dihydroisobenzofuran, already prepared from methyl dimethylaminobenzoylbenzoate. When condensed with dimethylaniline, the carbinol yields *o*-phenylbenzyl-di-(*p*-dimethylamino)triphenylmethane, m. p. 225°, described above, which when oxidised with chloroanil gives a compound, $(C_{36}H_{36}ON_2)_2 \cdot C_6Cl_4O_2$, m. p. 180° (decomp.), which is converted by alcoholic potassium hydroxide into *o*-phenylbenzyl-di-(*p*-dimethylamino)triphenylcarbinol,



m. p. 189°, giving a *hydrochloride*, m. p. 160–170° (decomp.). The original carbinol when condensed with diethylaniline gives *o*-phenylbenzyl-*p*-diethylamino-*p*-dimethylaminotriphenylmethane, $CHPh_2 \cdot C_6H_4 \cdot CH(C_6H_4 \cdot NEt_2) \cdot C_6H_4 \cdot NMe_2$, m. p. 150°, giving a *hydrochloride*, m. p. 170° (decomp.).

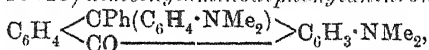
The *p*-dimethylaminobenzylbenzopinacone when heated with dilute sulphuric acid gives *p*-dimethylaminobenzylbenzoylbenzene, $COPh \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot NMe_2$, m. p. 69°, and this compound is also obtained if the sulphuric acid is replaced by benzoyl chloride or dimethylaniline, or if the pinacone is heated alone.

Methyl *p*-diethylamino-*o*-benzylbenzoate when treated with magnesium phenyl bromide only gives one compound, namely, *p*-diethylaminobenzyltriphenylcarbinol,



m. p. 114°, which with dimethylaniline gives *o*-phenylbenzyl-*p*-diethylamino-*p*-dimethylaminotriphenylmethane, m. p. 150 (see above).

In a further endeavour to confirm the constitution of some of the compounds described above, the author has studied the action of magnesium phenyl bromide on 3-dimethylaminoanthraquinone. If an excess of the anthraquinone is used, the product is 3-dimethylamino-9(or 10)-phenyloranthranol, $C_6H_4 \langle \begin{smallmatrix} CPh(OH) \\ CO \end{smallmatrix} \rangle C_6H_3 \cdot NMe_2$, m. p. 270°, which gives a *methyl ether*, m. p. 183°, an *ethyl ether*, m. p. 169°, and condenses with dimethylaniline, giving 3-dimethylamino-9 : 9(or 10 : 10)-dimethylaminodiphenylanthrone,

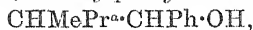


m. p. 205°. With an excess of magnesium phenyl bromide, the anthraquinone yields 3-dimethylamino-9 : 10-diphenylanthracene, $C_6H_4 \langle \begin{smallmatrix} CPh \\ CPh \end{smallmatrix} \rangle C_6H_3 \cdot NMe_2$, m. p. 264°, which when reduced with sodium amalgam in alcoholic solution gives 3-dimethylamino-9 : 10-diphenyldihydroanthracene, $C_6H_4 \langle \begin{smallmatrix} CHPh \\ CHPh \end{smallmatrix} \rangle C_6H_3 \cdot NMe_2$, m. p. 240°.

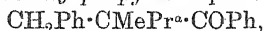
W. G.

Syntheses by means of Sodamide. Preparation and Study of New Mono- and Di-ketones. PHILIPPE DUMESNIL (*Ann. Chim.*, 1917, [ix], 8, 70–116).—For the most part a résumé

of work already published (compare A., 1911, i, 718; 1913, i, 877). The following new compounds are described: *methylpropylacetophenone*, $\text{CHMePr}^{\alpha}\cdot\text{COPh}$, b. p. $244^{\circ}/760$ mm., $128^{\circ}/15$ mm., giving an *oxime*, m. p. 76° ; α -phenyl- β -methylbutyl alcohol, $\text{CHMeEt}\cdot\text{CHPh}\cdot\text{OH}$, b. p. $120^{\circ}/13$ mm., giving an *acetate*, b. p. $123^{\circ}/10$ mm.; α -phenyl- β -methylpentyl alcohol,



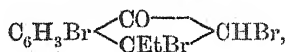
b. p. $126\text{--}127^{\circ}/12$ mm., giving an *acetate*, b. p. $136^{\circ}/13$ mm.; α -phenyl- β -ethylpentyl alcohol, $\text{CHEtPr}^{\alpha}\cdot\text{CHPh}\cdot\text{OH}$, b. p. $134^{\circ}/11$ mm., giving an *acetate*, b. p. $144^{\circ}/12$ mm. *Methylethylacetophenoneoxime*, m. p. 82° ; *ethylpropylacetophenoneoxime*, b. p. $150^{\circ}/25$ mm. *Benzylmethylpropylacetophenone*,



b. p. $235^{\circ}/40$ mm. β -Benzylbutane, $\text{CH}_2\text{Ph}\cdot\text{CHMeEt}$, b. p. $102^{\circ}/15$ mm. α -Benzyl- α -methylvaleramide, $\text{CH}_2\text{Ph}\cdot\text{CMePr}^{\alpha}\cdot\text{CONH}_2$, m. p. 81° , giving the corresponding *acid*, m. p. 47° . β -Benzylpentane, $\text{CH}_2\text{Ph}\cdot\text{CHMePr}^{\alpha}$, b. p. $110^{\circ}/25$ mm. W. G.

Alkylated Indones. R. STOERMER and E. LAAGE (*Ber.*, 1917, 50, 981—989).—A number of alkylated indones have been prepared by dissolving the *allo*-modifications of some alkylcinnamic acids in sulphuric acid containing a little anhydride and pouring the product on ice. The indones are accompanied by the stable forms of the acids, but can be separated by extraction from alkaline solutions. They are highly coloured oils, and usually possess very pungent odours, reminiscent of acraldehyde, which they also resemble in changing into resinous and solid polymerides when kept.

allo- β -Methylcinnamic acid yields 3-methylindone, b. p. $140\text{--}141^{\circ}/19$ mm., which forms a yellow *semicarbazone*, m. p. $208\text{--}216^{\circ}$ (decomp.), and reacts with bromine in carbon disulphide to give a di-substitution product, namely, 2:6(?)*-dibromo-3-methylindone*, in orange-coloured needles, m. p. $157\text{--}157.5^{\circ}$. 3-Ethylindone, b. p. $158\text{--}159^{\circ}/20$ mm., m. p. 43.5° , yields a *semicarbazone*, lemon-yellow leaflets, m. p. 177.5° , and combines with bromine to form 2:3:6(?)*-tribromo-3-ethylhydrindone*,



which crystallises in colourless leaflets, and changes when heated into 2:6(?)*-dibromo-3-ethylindone*, orange-coloured leaflets, m. p. 108.5° .

2-Methylindone (A., 1915, i, 685) reacts with magnesium methyl iodide to form 1:2-dimethylinden-1-ol, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe}\cdot\text{OH} \\ \diagup \quad \diagdown \\ \text{CH}\cdot\text{CMe} \end{array}$, which crystallises in small, quadratic leaflets, m. p. $82\text{--}82.5^{\circ}$, b. p. $117^{\circ}/9$ mm., and may be reduced to 1:2-dimethylindan-1-ol (1-hydroxy-1:2-dimethylhydrindene), m. p. $39\text{--}40^{\circ}$, b. p. $108.5^{\circ}/8$ mm. This carbinol is more easily obtained from 2-methylhydrindone, as this is readily prepared from β -phenyl- α -methylpropionyl chloride. It

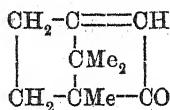
gives various colour reactions with sulphuric and nitric acids, and very readily loses the elements of water, for example, by boiling with 5% sulphuric acid, changing thereby into 2:3-dimethylindene. This is a pale yellow oil, m. p. 11° , b. p. $113-114^{\circ}/21$ mm., which forms an orange-red *picrate*, m. p. $86-87^{\circ}$.

3-Methylindene is also more easily prepared by this scheme than by any other. Hydrindone is converted by the Grignard reaction into 1-hydroxy-1-methylhydrindene, m. p. 57° (A., 1913, i, 1364), and this is boiled with dilute sulphuric acid. J. C. W.

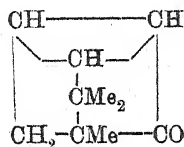
Action of Organo-magnesium Compounds on, and Reduction of, Cineol. C. F. VAN DUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, 20, 66-68).—Cineol gives an additive compound with magnesium methyl iodide, which when heated at 160° decomposes violently with vigorous evolution of a gas, and a liquid distils over (compare Grignard, *Bull. Soc. chim.*, 1903, [iii], 29, 944). This liquid is now shown to be a mixture of hydrocarbons, b. p. $170-178^{\circ}/759$ mm., having the composition $C_{10}H_{16}$. It can be separated into three fractions, having (1) b. p. $170-172.5^{\circ}$, D_{16}^{20} 0.841; n_D^{16} 1.4679; (2) b. p. $172.5-175^{\circ}$, D_{16}^{20} 0.846, n_D^{16} 1.4706; (3) b. p. $175-178^{\circ}$, D_{16}^{20} 0.853, n_D^{16} 1.4752. A similar, but less vigorous, reaction takes place with magnesium ethyl bromide. With magnesium phenyl bromide the action is quite different, the additive compound not being decomposed by heat.

Attempts to reduce cineol by passing its vapour along with hydrogen over finely divided nickel at 170° were not successful. W. G.

β -pericycloCamphanone [Angeli's Camphenone, Schiff's Dehydrocamphor]. J. BREDT and WILHELM HOLZ (*J. pr. Chem.*, 1917, [ii], 95, 133-159).—The substance obtained by Schiff (A., 1882, 527) and Angeli (A., 1895, i, 61, 382) by the elimination of a molecule of nitrogen from diazo-camphor was regarded by the latter investigator as camphenone of structure I, but evidence is now adduced in support of formula II, for which the descriptive name β -pericyclocamphanone is suggested; the term *peri* is used in analogy with the structure of naphthalene, indicating the position of the bridge which completes the trimethylene ring, this position being still further defined by the letter β :



(I.)

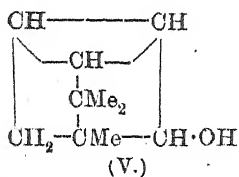
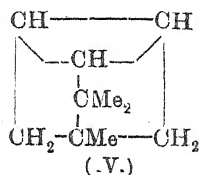


(II.)

β -pericycloCamphanone (*semicarbazone*, needles, m. p. $243-244^{\circ}$) was prepared from camphorquinone by successive conversion into camphorquinone hydrazone (Forster and Zimmerli, T., 1910, 97, 2156) and diazo-camphor, the liberation of nitrogen from the last

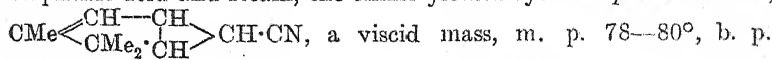
substance being aided by the presence of copper-bronze powder. In acetic acid solution it gradually formed a *hydrobromide* (annexed formula, III), m. p. 113—114°, $[\alpha]_D^{25} + 13.23^\circ$ in benzene, which on reduction yielded ordinary camphor. Contrary to Angeli's views, β -*pericyclocamphanone* does not react with bromine in carbon disulphide or chloroform, except under the influence of sunlight.

By conversion of β -*pericyclocamphanone* into its *hydrazone*, m. p. near 45°, b. p. 143—148°/33 mm., and subsequent decomposition with alcoholic sodium ethoxide at 190°, *pericyclocamphane* (annexed formula, IV.), m. p. 117—118°, b. p. 150—152°, was obtained as an optically inactive substance which did not react with bromine in carbon disulphide or chloroform, and is possibly identical with Wagner's β -bornylene. The reduction product of β -*pericyclocamphanone* with sodium and alcohol was not borneol, as Angeli believed, but an isomeric β -*pericyclocamphanol*, m. p. 174—176°, b. p. 205—208°, $[\alpha]_D^{20} + 39.69^\circ$ in benzene (annexed formula, V.); *phenylurethane*,



$\text{C}_{10}\text{H}_{15}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$, needles, m. p. 106—108°; *methyl xanthate* derivative, $\text{C}_{10}\text{H}_{15}\cdot\text{O}\cdot\text{CS}_2\text{Me}$, colourless needles, m. p. 49—51°; *chloride*, $\text{C}_{10}\text{H}_{15}\text{Cl}$, m. p. near 130°, obtained by the action of phosphorus pentachloride in light petroleum; the *methyl ether*, $\text{C}_{10}\text{H}_{15}\cdot\text{OMe}$, prepared by successive treatment of the ethereal solution with sodium and methyl sulphate, had b. p. 189—190°, or 79—80°/16 mm., $[\alpha]_D^{20} + 57.96^\circ$, $D_4^{25} 1.094208$, $n_D^{25} 1.4654$, and was quite distinct from *d*-bornyl methyl ether, b. p. 193—194°/760 mm., or 76—77°/14 mm., $[\alpha]_D^{20} + 57.57^\circ$, $D_4^{25} 1.09261$, $n_D^{25} 1.46479$, the exaltation in the molecular refraction of the former substance being insufficient for the presence of an ethylenic linking and in accordance with the expected increment for a trimethylene ring.

Confirmatory evidence of the presence of the trimethylene ring in β -*pericyclocamphanone* was obtained by the degradation of its *oxime*, tablets, the indefinite m. p., 80—127°, of which was probably due to the presence of stereoisomerides. When treated with diluted sulphuric acid and steam, the oxime yielded *cyclocamphenonitrile*,



111—111.5°/17 mm., of unpleasant odour, which by prolonged treatment with alcoholic potassium hydroxide was convertible into the corresponding *cyclocamphenonic acid*, $\text{C}_{10}\text{H}_{14}\text{O}_3$, leaflets, m. p. 108—110°; *ethyl ester*, b. p. 111—112°/14.5 mm., $[\alpha]_D^{25} - 105.98^\circ$, $D_4^{25} 1.097936$, $n_D^{25} 1.47376$, the spectrochemical characteristics of which were in accord with the presence of the trimethylene ring and the double bond. Oxidation of the *cyclocamphenonic acid* with

potassium permanganate in neutral solution gave rise to cycloisocamphoric acid, $\begin{matrix} \text{CH}(\text{CO}_2\text{H}) \\ | \\ \text{CH}(\text{CO}_2\text{H}) \end{matrix} > \text{CH} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$, crystalline scales, m. p. 228—230°.

The constitution now suggested for β -pericyclocamphanone also gains probability from structural considerations, which indicate a difficulty in the formation of a double bond at either of the carbon atoms common to the two ring systems of the camphor molecule.

D. F. T.

Cerebrosides. III. Conditions for Hydrolysis of Cerebrosides. P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1917, **31**, 627—634).—For the estimation of the sugar in a cerebroside, the most favourable conditions for hydrolysis seem to be to heat 1 gram of the cerebroside with 16 c.c. of 3% sulphuric acid with shaking in a sealed tube for twelve hours at 105°. Approximately 90% of the sugar present in the cerebroside is thus obtained. When the base and fatty acids are to be estimated, the heating should be continued for twenty-four hours. Detailed instructions are given for the isolation of cerebronic and lignoceric acids from the resulting hydrolytic products.

H. W. B.

Cerebrosides. IV. Kerasin. P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1917, **31**, 635—647. Compare this vol., i, 525).—The authors have prepared and examined the acetyl, benzoyl, cinnamoyl, and *p*-nitrobenzoyl derivatives of phrenosin and kerasin with the view of employing them for the separation of these cerebrosides.

Hexa-acetylphrenosin, $\text{C}_{60}\text{H}_{105}\text{O}_{15}\text{N}$, has m. p. 41—43°, $[\alpha]_D^{20} - 11.07^\circ$; Thierfelder (*A.*, 1914, i, 339) gives m. p. 39—41°, $[\alpha]_D^{17} - 3^\circ$. Penta-acetylkerasin, $\text{C}_{57}\text{H}_{101}\text{O}_{13}\text{N}$, melts at 54—56°, $[\alpha]_D^{20} - 16.46^\circ$. Tribenzoylphrenosin, $\text{C}_{69}\text{H}_{105}\text{O}_{12}\text{N}$, is prepared by the action of benzoyl chloride on phrenosin in pyridine solution. It is obtained in crystalline form from methyl alcohol, m. p. 65—66°, $[\alpha]_D^{20} + 21.2^\circ$. On decomposing with sodium methoxide, phrenosin is readily obtained. Tricinnamoylphrenosin, $\text{C}_{75}\text{H}_{111}\text{O}_{12}\text{N}$, and tri-*p*-nitrobenzoylphrenosin, $\text{C}_{69}\text{H}_{102}\text{O}_{18}\text{N}_4$, are prepared in a similar way. The former has m. p. 69—70°, $[\alpha]_D^{20} + 21.72^\circ$, and the latter m. p. 94—96°, $[\alpha]_D^{20} + 12.18^\circ$.

H. W. B.

Cerebrosides. V. Cerebrosides of the Kidney, Liver, and Egg Yolk. P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1917, **31**, 649—654. Compare this vol., i, 525).—The composition of the cerebrosides of the kidney, liver, and egg yolk seems to be identical with that of the cerebrosides obtained from the nerve tissue. They contain the same sugar, galactose, the same base, sphingosine, and the same fatty acids, lignoceric and cerebronic.

H. W. B.

Synthesis of Mandelonitrile-glucoside, Sambunigrin, and similar Substances. EMIL FISCHER and MAX BERGMANN (*Ber.*, 1917, **50**, 1047—1069).—The discovery of more and more cyanogenic glucosides, in ever-widening botanical species, has led botanists and chemists to speculate on the rôle of hydrogen cyanide in nitro-

gen assimilation. The synthesis of such glucosides gains, thereby, added interest, and, after failing in the case of glycollic acid to reach a further stage than the production of the glucosidoglycollamide, $\text{NH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_{11}\text{O}_5$ (A., 1911, i, 802), success has now been achieved in the case of mandelic acid. The chemical history of mandelonitrile-glucoside is reviewed.

Dry, molten ethyl *dl*-mandelate is shaken with acetobromoglucose and silver oxide and so converted into a mixture of the *ethyl tetra-acetylglucosidomandelates*, which crystallises in concentric groups of needles, with fluctuating m. p. ($102\text{--}109^\circ$) and rotation ($[\alpha]_{\text{D}} - 33^\circ$ to -40°). The mixture is converted into the un-acetylated amides by means of methyl-alcoholic ammonia, and these are separated by crystallisation from a mixture of pyridine and ethyl acetate. A pyridine compound of *l*-mandelamideglucoside crystallises out, and this loses pyridine in a warm vacuum desiccator and on solution in water, leaving the pure amide as a glassy mass. The *isomeride* is also a viscous mass. Both are converted into crystalline tetra-acetates by treatment with acetic anhydride and pyridine. *l*-Tetra-acetylglucosidomandelamide forms microscopic needles, m. p. 161° (corr.), $[\alpha]_{\text{D}}^{19} - 89\cdot53^\circ$, in acetone, and the *d*-*isomeride*, $\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4\cdot\text{O}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in felted needles, m. p. $136\text{--}137^\circ$ (corr.), $[\alpha]_{\text{D}}^{18} - 16\cdot53^\circ$, in acetone. These are dehydrated to the nitriles by warming with phosphoryl chloride. The *l*-tetra-acetylglucosidomandelonitrile is obtained in rosettes of long, flat needles, m. p. $139\text{--}140^\circ$ (corr.), $[\alpha]_{\text{D}}^{25} - 24\cdot01^\circ$, agreeing, therefore, with the tetra-acetate of natural *l*-mandelonitrileglucoside (see especially Power and Moore, T., 1909, 95, 259), and the *d*-*isomeride*, prismatic needles, m. p. $125\text{--}126^\circ$ (corr.), $[\alpha]_{\text{D}}^{22} - 52\cdot5^\circ$, coincides with the tetra-acetate of sambunigrin.

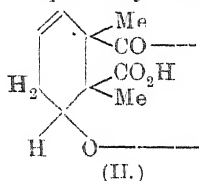
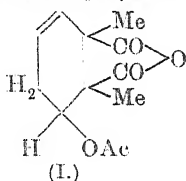
These tetra-acetates are hydrolysed by means of warm methyl-alcoholic ammonia, but racemisation takes place and the product is *dl*-mandelonitrile-glucoside, identical with natural prulaurasin (see especially Caldwell and Courtauld, T., 1907, 91, 671). The mixture can be separated by crystallisation from a mixture of amyl alcohol and benzene (1:6). *d*-Mandelonitrile-glucoside, m. p. $151\text{--}152\cdot5^\circ$ (corr.), $[\alpha]_{\text{D}}^{15} - 76\cdot3^\circ$, identical with sambunigrin (Bourquelot and Danjou, A., 1905, i, 912), crystallises out, and *l*-mandelonitrile-glucoside, m. p. $149\text{--}150^\circ$ (corr.), $[\alpha]_{\text{D}}^{21} - 27\cdot0^\circ$, may be recovered from the mother liquor. Both glucosides are hydrolysed under the influence of emulsin, which is surprising, unless it is due to the rearrangement of one into the other *isomeride* by the enzyme.

Amygdalin is easily acetylated by means of acetic anhydride and pyridine, and the hepta-acetate, m. p. $171\text{--}172^\circ$ (corr.) (Caldwell and Courtauld, *loc. cit.*), may be hydrolysed to amygdalin again by means of methyl-alcoholic ammonia.

Glucosidoglycollamide (A., 1911, i, 802) may be converted by means of acetic anhydride and pyridine into a *tetra-acetate*, $\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2\cdot\text{H}_2\text{O}$, m. p. $135\text{--}136^\circ$, and again at $155\text{--}156^\circ$ (corr.), $[\alpha]_{\text{D}}^{20} - 23\cdot83^\circ$, and this forms *tetra-acetylglucosidoglycollonitrile*, $\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CN}$, hexagonal plates, m. p. $129\text{--}130^\circ$ (corr.), $[\alpha]_{\text{D}}^{18} - 38\cdot63^\circ$, when warmed with phosphoryl

chloride. The acetate may be hydrolysed by means of methyl-alcoholic ammonia, but so far the expected glycollonitrile-glucoside has only been obtained as a syrup. J. C. W.

Cantharidin. VI. *iso*Cantharidin. J. GADAMER (*Arch. Pharm.*, 1917, 255, 277—290. Compare Rudolph, this vol., i, 468).—The formula of cantharidin advocated by Rudolph (*loc. cit.*) explains all the known facts except two: first, the formation of α -hemineillic acid by the pyrogenic decomposition of barium cantharate, and secondly, the properties of *isocan*tharidin and of *isocan*tharidic acid. The second discrepancy is now removed by the author's discovery that *isocan*tharidin and *isocan*tharidic acid do not exist, the substances described by Anderlini and Ghira in 1891 under these names being in reality *acetylhydratocan*tharic anhydride (I) and *acetylhydratocan*tharic acid respectively. The proof is



as follows. Accepting Rudolph's formula of cantharidin, cantharic acid must have formula II. *d*-Cantharic acid, $[\alpha]_D + 87.5$ — 90° , was heated with acetyl chloride at 135° for three hours. The yield of the resulting "*isocan*tharidin" was 120% of the theoretical, calculated on the formula $C_{10}H_{12}O_4$, and about 100% calculated on the formula $C_{12}H_{14}O_5$. The product after removal of a little *d*-cantharic acid, had $[\alpha]_D -100$ to -101.25° in acetone ($c=2$), and in its other properties agreed with Anderlini and Ghira's "*isocan*tharidin," except that the m. p. was 84 — 85° , sintering at 80.5° . It contains one acetyl group and behaves like an acid anhydride during titration. It readily combines with $1H_2O$, yielding acetylhydratocanthalic acid, which behaves as a dibasic acid and readily reverts to the anhydride by loss of water.

Anderlini and Ghira state that the barium salt is a specially characteristic derivative of "*isocan*tharidin." The author has therefore prepared this derivative of his levorotatory compound, and finds that its properties agree with those recorded by Anderlini and Ghira; the analytical data, however, correspond with the formula $C_{12}H_{14}O_6 \cdot Ba \cdot 3H_2O$, not with $C_{10}H_{12}O_5 \cdot Ba \cdot 5H_2O$.

Dankworth has observed (*Arch. Pharm.*, 1914, 252, 680) that the product of the hydrolysis of "*isocan*tharidin" (acetylhydratocanthalic anhydride) is not pure *d*-cantharic acid, since the $[\alpha]_D$ value is only $+60.7$ to $+60.8^\circ$. The author shows that this is due to incomplete hydrolysis; when *l*-acetylhydratocanthalic anhydride is hydrolysed by boiling water for several days the only product which can be isolated is *d*-cantharic acid, $[\alpha]_D + 87.5^\circ$. C. S.

Cantharidin. VII. Reduction Products of Cantharic Acid and Hydrobromocanthalic Acid. J. GADAMER (*Arch. Pharm.*, 1917, 255, 290—302).—In consequence of the genetic

relationships recorded in this paper, the author re-names *d*-cantharic acid ($[\alpha]_D + 87.5^\circ$ to 90°) *l*-cantharic acid.

When *l*-cantharic acid dissolved in rather more than the calculated quantity of sodium carbonate solution is reduced by Mannich's modification of the Paal-Skita method, only one product is formed, namely, *l*-dihydrocantharic acid, $C_{10}H_{14}O_4$, m. p. $264-267^\circ$, $[\alpha]_D - 52.5^\circ$ in alcohol ($c=2$). The production of only one acid is regarded by the author as evidence in favour of the constitution of *l*-cantharic acid already recorded (preceding abstract), and therefore also of Rudolph's formula of cantharidin.

r-Cantharic acid, when reduced by the Paal-Skita method, yields *r*-dihydrocantharic acid, $C_{10}H_{14}O_4, \frac{1}{4}H_2O$, m. p. $264.5-265^\circ$, which can be partly resolved by means of the brucine salt; the *l*-acid thus obtained has $[\alpha]_D - 33^\circ$ to -35° . The same *l*-dihydrocantharic acid is obtained, together with a number of other, unexamined products, when *l*-hydrobromocantharic acid is reduced by zinc and hydrochloric acid.

When an alkaline solution of *l*-cantharic acid in aqueous sodium hydroxide is energetically reduced by hydrogen and palladium (on bone charcoal), *l*-dihydrocantharic acid and deoxycantharidin (or its hydrate, deoxycantharidic acid) are produced. The latter is optically inactive and agrees in all its properties with the deoxycantharidin obtained from the "dibromide" by Rudolph (this vol., i, 468).

The author has obtained evidence which seems to indicate the existence of a second modification of deoxycantharidin, which is amorphous, sinters strongly at 100° , and is completely molten at about 115° .
C. S.

Bixins. I. J. RINKES and J. F. B. VAN HASSELT (*Chem. Weekblad*, 1917, 14, 888-894. Compare A., 1916, i, 425, 829).—One of the decomposition products of methylbixin ozonide is a liquid of agreeable odour, b. p. $52-60^\circ/9$ mm. It yields a *monosemicarbazone*, m. p. 261° ; a *phenylosazone*, m. p. 170° ; a *phenylmethylosazone*, m. p. 178° ; a condensation product with Braun's reagent, m. p. 260° ; and a *dioxime*, m. p. 187° . It is a dialdehyde of the formula $C_5H_6O_2$. The dibasic acid produced by oxidation with water and silver oxide is too soluble in water to admit of its extraction by ether.

Another decomposition product yields a *semicarbazone*, m. p. 218° , and a condensation product with Braun's reagent, m. p. 187° . It is an aldehyde of the formula $C_8H_{10}O_3$, and on oxidation is converted into a methoxy-derivative, $C_8H_{10}O_4$, m. p. 121° , which is the monomethyl ester of a dibasic acid, $C_7H_8O_4$, m. p. 231° (decomp.). On reduction by Paal and Skita's method, this acid takes up four hydrogen atoms, forming a compound, $C_7H_{12}O_4$, m. p. $93-94^\circ$, which is probably inactive β -methyldipic acid.

A. J. W.

Pyrylium Compounds. III. W. DILTHEY (*Ber.*, 1917, 50, 1008-1010. Compare A., 1916, i, 829; *J. pr. Chem.*, 1917, [ii], 95, 107).—The pyrylium compounds described in the earlier papers

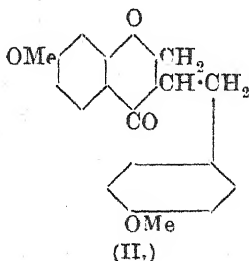
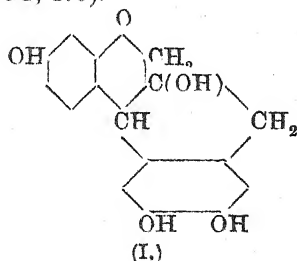
were substituted in position 4. The cinnamylidene derivatives of ketones yield pyrylium compounds in which no substituent is present in this position. Thus, when a solution of phenyl cinnamylidenemethyl ketone in a mixture of acetic acid and acetic anhydride is boiled with ferric chloride, 2:6-diphenylpyryl ferrichloride, $\text{CH} \begin{smallmatrix} \text{CH:CPh} \\ \text{CH}\cdot\text{CPh} \end{smallmatrix} \text{OCl,FeCl}_3$, is formed. This crystallises in yellow prisms, m. p. 185—186° (corr), exhibits an intense blue fluorescence when dissolved in much acidified water, and yields 2:6-diphenylpyridine when treated with ammonia. Similarly, anisyl cinnamylidenemethyl ketone gives 2-anisyl-6-phenylpyryl ferrichloride, which crystallises in slender, brownish-yellow needles, m. p. 181° (corr.), and exhibits a strong, greenish-yellow fluorescence in solutions. A mixture of styryl phenyl ketone and styryl methyl ketone, under the same treatment, yields 6-styryl-2:4-diphenylpyryl ferrichloride, in reddish-yellow needles, m. p. 266° (corr.). J. C. W.

Action of Phthalic Anhydride on 1:6-Dihydroxynaphthalene. Formation of 6:6'-[3:11]-Dihydroxynaphthfluoran.

II. O. FISCHER and E. KÖNIG (*Ber.*, 1917, 50, 1011—1015. Compare A., 1914, i, 712).—During the preparation of 3:11-dihydroxynaphthfluoran by the condensation of phthalic anhydride and 1:6-dihydroxynaphthalene, a small quantity of an intermediate product, o-1:6-dihydroxy-2-naphthoylbenzoic acid, may be isolated, in very pale yellow needles or prisms, m. p. 220—221°. It may be converted by means of methyl sulphate into methyl o-1:6-dimethoxy-2-naphthoylbenzoate, m. p. 141—142°, and this hydrolysed to the free acid, m. p. about 214°.

3:11-Dihydroxynaphthfluoran reacts with the halogens in glacial acetic acid solution; the dichloride, $\text{C}_{28}\text{H}_{14}\text{O}_3\text{Cl}_2$, crystallises in colourless needles, decomp. 280°; the dibromide forms stellate groups of prisms, and the diiodide is very similar. A dinitro-compound, yellow needles, has also been isolated. J. C. W.

Chromanones. The Brazilin Question. I. PAUL PFEIFFER and JOSEPH GRIMMER (*Ber.*, 1917, 50, 911—927).—Pfeiffer is attempting to support his formula for brazilin (I) by synthesis, and has so far been able to prepare a compound of the formula II (compare *Chem. Zeitsch.*, 1904, 3, 420; Perkin and Robinson; T., 1908, 93, 493).



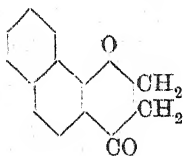
The first stage consisted in the synthesis of 7-methoxychromanone, and as a preliminary attempt with this end in view, 2-hydroxy-4-methoxyacetophenone (pæonol) was condensed with formaldehyde in the presence of sulphuric acid. The product obtained, however, was 4:4'-*dihydroxy*-2:2'-*dimethoxy*-5:5'-*diacetyldiphenylmethane*, which crystallises in glistening needles, m. p. 197°, and forms a *dioxime*, m. p. 241° (decomp.), and a *diacetate*, m. p. 180°. *m*-Dimethoxybenzene behaves similarly with formaldehyde, yielding 2:2':4:4'-*tetramethoxydiphenylmethane*, m. p. 149°.

The chromanone was finally obtained by reducing 7-methoxychromone by means of hydrogen and platinum-black. This compound is best obtained by Kostanecki's method (A., 1902, i, 304), and is characterised by a *semicarbazone*, m. p. 218° (decomp.).

7-Methoxychromanone [7-methoxy-2:3-dihydro- γ -benzopyrone], $\text{OMe} \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{O}-\text{CH}_2 \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$, crystallises in colourless needles, m. p. 58°, and forms a *semicarbazone*, m. p. 226—227° (decomp.), and an *oxime*, large needles, m. p. 137°. It also reacts with amyl nitrite and hydrochloric acid to form 3-oximino-7-methoxychromanone [3-oximino-7-methoxy-2:3-dihydro- γ -benzopyrone], a yellow powder, m. p. 169°, and it condenses with anisaldehyde to form the 3-anisylidene derivative. This crystallises in pale yellow, glistening leaflets, m. p. 134°, gives a deep orange-red solution in concentrated sulphuric acid, and may be reduced to 7:4'-*dimethoxy*-3-benzylchromanone [7:4'-*dimethoxy*-3-benzyl-2:3-dihydro- γ -benzopyrone], $\text{OMe} \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{O}-\text{CH}_2 \\ \text{CO} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \end{smallmatrix}$, leaflets, m. p. 68—70°.

Some chromanones of the naphthalene series have also been prepared.

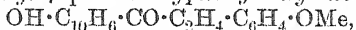
α -Naphthachromone [α -naphtha- γ -pyrone] (Kostanecki, A., 1902, i, 303) is conveniently obtained by the condensation of 2-acetyl- α -naphthol with ethyl formate in the presence of powdered sodium. It crystallises in silky needles, m. p. 125°, forms a *semicarbazone*, m. p. 256° (decomp.), and may be reduced to α -naphthachromanone [2:3-dihydro- α -naphtha- γ -pyrone] (annexed formula). This crystallises in brilliant, rhombic, colourless tablets, m. p. 104·5°, which dissolve in sulphuric acid with a golden-yellow colour, and forms an *oxime*, m. p. 144—144·5°, a *semicarbazone*, m. p. 259—260° (decomp.), and a 3-anisylidene compound, pale yellow needles, m. p. 144—145°, which give a deep red solution in sulphuric acid.



Neither ethyl α -naphthachromone-2-carboxylate (pale brown, stout needles, m. p. 135°; for the acid, see *ibid.*) nor α -naphthachromanone, m. p. 167° (Kostanecki, A., 1898, i, 373), can be reduced by means of hydrogen and platinum-black.

2-Acetyl- α -naphthol condenses with anisaldehyde in the presence of sodium hydroxide to form 1-hydroxy-2-naphthyl *p*-methoxystyryl

ketone, orange-red needles, m. p. 160°, which may be reduced to 1-hydroxy-2-naphthyl β -p-methoxyphenylethyl ketone,



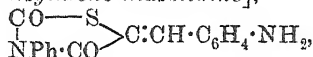
very long, pale yellow needles, m. p. 114°.

J. C. W.

Substituted Rhodanines and some of their Aldehyde Condensation Products. XIII. RUDOLF ANDREASCH (*Monatsh.*, 1917, **38**, 121—139).—The condensation of rhodanines and related ring systems with aldehydes is illustrated by still further examples (compare Stieger, this vol., i, 171).

3-Phenylrhodanine and *p*-aminobenzaldehyde condense in warm acetic acid to form 3-phenyl-5-*p*-aminobenzylidenerrhodanine, $\text{CS} \text{---} \text{S} \begin{array}{l} \diagup \\ \diagdown \end{array} \begin{array}{l} \text{NPh} \cdot \text{CO} \\ \text{C} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \end{array}$, which crystallises in dichromate-coloured, filamentous needles, m. p. 227—228°, and dyes skin, wool, or silk yellow.

Phenylthiocarbimideglycollide and *p*-aminobenzaldehyde form *v*-phenyl- β -*p*-aminobenzylidenethiocarbimideglycollide [2 : 4-diketo-3-phenyl-5-*p*-aminobenzylidenethiazolidine],

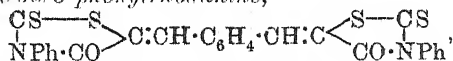


as a yellow, crystalline powder, m. p. 246°. The corresponding benzylidene compound forms colourless needles, m. p. 239°, and the *o*-hydroxybenzylidene compound crystallises in pale yellow, woolly masses, m. p. 140°.

Phenylthiohydantoin yields *v*-phenyl- β -benzylidenesisothiohydantoin [2-imino-4-keto-3-phenyl-5-benzylidenethiazolidine], m. p. 255—256°, which has the appearance of lead iodide. The corresponding salicylidene compound has m. p. 244°.

Protocatechualdehyde and 3-phenylrhodanine form 3-phenyl-5-*mp*-dihydroxybenzylidenerrhodanine, in bright yellow needles, m. p. above 260°. This behaves like an indicator, for aqueous suspensions give very deep violet solutions with alkali hydroxides, which become yellow again on neutralisation. The compound is in many other respects like alizarin; it is a vat dye, but does not give nice shades. The corresponding 5-*op*-dihydroxybenzylidene compound is an orange-yellow, crystalline powder, m. p. about 350°, which gives carmine-red solutions with traces of alkali hydroxide. 3-Tolyl-5-*op*-dihydroxybenzylidenerrhodanine is a dirty orange-yellow powder, m. p. about 200°, and the corresponding 3- β -naphthyl compound has m. p. 190—200°.

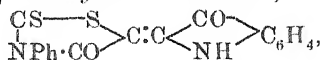
3-Phenylrhodanine and isophthalaldehyde condense to form 5-isophthalylidene-bis-3-phenylrhodanine,



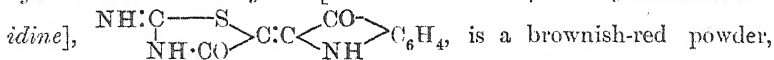
which crystallises from ethyl benzoate in chrome-yellow crusts, m. p. above 360°. The simple rhodanine gives the corresponding 5-isophthalylidene-bis-rhodanine, m. p. 260—265° (decomp.).

3-Phenyl-5-*m*-carboxybenzylidenerrhodanine is a cadmium-yellow powder, m. p. 347—348° or higher.

Phenylrhodanine and the related ring systems also condense with isatin. 3-Phenyl-5- ψ -indoxylidenethiodaniline,



crystallises as a purple-red, shimmering scale, m. p. 260°. "isoThiohydantoin-2-indolindigo" [2-imino-4-keto-5- ψ -indoxylidenethiazolidine],



is a brownish-red powder, m. p. above 360°. 2:4-Diketo-5- ψ -indoxylidenethiazolidine is an orange-yellow powder, m. p. above 370°. "5- ψ -Indoxylrhodanine" is identical with Felix and Friedländer's "5-thiazolthiol-2-indole-indigo" (A., 1910, i, 278). J. C. W.

A Theory of the Mechanism of the Phytochemical Synthesis of certain Alkaloids. ROBERT ROBINSON (T., 1917, 111, 876—899).—Starting with ammonia, formaldehyde, ornithine, lysine, and degradation products of carbohydrates, it is shown how many alkaloids might be built up by reactions possible and probable to the living plant, namely, aldol condensations, and condensations of carbinol-amines containing the system $\text{OH} \cdot \dot{\text{C}} \cdot \dot{\text{N}}$ with aldehydes or ketones, oxidations and reductions, eliminations of water, and methylations by means of formaldehyde. The theory is discussed with reference to the pyrrolidine, piperidine, quinuclidine, and isoquinoline (morphine, berberine, narcotine, corydaline, etc.) groups, and should stimulate chemists to much valuable work in these fields. J. C. W.

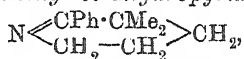
Preparation of Compounds of Alkaloids of the Morphine Group. SOC. CHEM. IND. IN BASLE (Brit. Pat., 107409, 1916 from J. Soc. Chem. Ind., 1917, 36, 979).—Alkaloids of the morphine group, or their derivatives, are caused to react in equimolecular proportions with CC-diallylbarbituric acid, a CC-allylalkylbarbituric acid, or a CC-dialkylbarbituric acid, giving well-crystallised compounds with valuable therapeutic (soporific or sedative) properties. H. W.

Highly Active Vitamine Preparation thoroughly Freed from Inactive Ingredients. SOC. CHEM. IND. IN BASLE (U.S. Pat., 1235198, 1917; from J. Soc. Chem. Ind., 1917, 36, 1064).—Organic food products are extracted with dilute alcohol and the alcohol removed from the extract by distillation in a vacuum. The aqueous solution of the extract is treated successively in acid condition with lead acetate and in neutral condition with basic lead acetate for the removal of impurities. After the solution has been freed from lead, it may be evaporated to dryness or may be first further purified by treatment with an alkaloid precipitant, decomposition of the precipitate, and re-solution of the alkaloid. The resulting vitamine products are yellowish-brown, hygroscopic substances, soluble in water-forming solutions faintly acid to litmus, and giving with

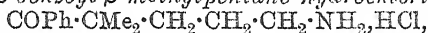
alkalis yellow solutions with a strong odour of methylamine. The aqueous solutions give precipitates with tannin, silver nitrate, and phosphomolybdic and phosphotungstic acids, the last of which gives characteristic colour reactions with sodium carbonate and diazobenzenesulphonic acid.

H. W.

Syntheses by means of Sodamide. V. Preparation of δ -Aminoketones and of 2-Phenyl-3:3-dialkyltetrahydropyridines. A. HALLER and (MME.) RAMART-LUCAS (*Ann. Chim.*, 1917, [ix], 8, 5—21).—The sodium derivatives of the dialkylacetophenones, $\text{COPh}\cdot\text{CRR}'\text{Na}$, react with trimethylene chlorobromide, giving γ -chloropropyldialkylacetophenones, which with ammonia yield 2-phenyl-3:3-dialkyltetrahydropyridines. Thus, when ϵ -chloro- β -benzoyl- β -methylpentane (compare Haller and Bauer, A., 1911, i, 651) is heated in a sealed tube at 100° with alcoholic ammonia, it yields 2-phenyl-3:3-dimethyltetrahydropyridine,

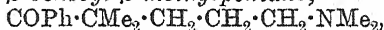


b. p. $150\text{--}151^\circ/17$ mm., a colourless liquid, which turns yellow in air. When heated with concentrated hydrochloric acid, this base gives ϵ -amino- β -benzoyl- β -methylpentane hydrochloride,



colourless prisms, m. p. 220° , giving a *platinichloride*. With dry hydrogen chloride in anhydrous ether, the tetrahydropyridine gives a compound, $\text{C}_{13}\text{H}_{18}\text{NCl}$, which is probably its hydrochloride.

When heated in a sealed tube at 100° with an alcoholic solution of dimethylamine, ϵ -chloro- β -benzoyl- β -methylpentane yields ϵ -dimethylamino- β -benzoyl- β -methylpentane,



b. p. $178\text{--}179^\circ/18$ mm., giving a *hydrochloride* and a *platinichloride*.

A similar series of compounds has been prepared from ζ -chloro- γ -benzoyl- γ -methylhexane, $\text{COPh}\cdot\text{CMeEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$, b. p. $175\text{--}180^\circ/14$ mm., of which the following are described: 2-phenyl-3-methyl-3-ethyltetrahydropyridine, b. p. $160\text{--}161^\circ/15$ mm., giving a *hydrochloride*; ζ -dimethylamino- γ -benzoyl- γ -methylhexane, giving a *hydrochloride*, m. p. 120° (decomp.), and a *platinichloride*.

ζ -Chloro- γ -benzoyl- γ -ethylhexane yielded ζ -amino- γ -benzoyl- γ -ethylhexane, giving a *platinichloride*, and ζ -dimethylamino- γ -benzoyl- γ -ethylhexane, giving a *platinichloride*.

ϵ -Chloro- β -benzoyl- β -methylpentane will react with silver acetate instead of ammonia, giving β -benzoyl- β -methylamyl acetate, $\text{COPh}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OAc}$, which on hydrolysis gives the corresponding *keto-alcohol*, m. p. 120° .

W. G.

The Compounds of Phenol and the Cresols with Pyridine.

W. H. HATCHER and F. W. SKIRROW (*J. Amer. Chem. Soc.*, 1917, 39, 1939—1977).—In the treatment of coal tar, it is already known that the crude phenols must be removed from the tar oils before the pyridine can be economically extracted with sulphuric acid.

c c*

By experiment it is now shown that although in an equimolecular solution of pyridine and phenol in benzene the extraction of pyridine and phenol by dilute sulphuric acid and sodium hydroxide respectively is almost unaffected by the presence of the second solute, a quadrimolecular proportion of phenol very greatly reduces the extraction of pyridine by dilute sulphuric acid, although a quadrimolecular proportion of pyridine causes only a slight reduction in the percentage extraction of the phenol by dilute sodium hydroxide.

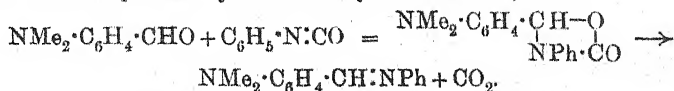
An examination of the compounds formed by pyridine with phenol, *o*-cresol, and *p*-cresol respectively, confirms the results already published by Bramley (T., 1916, 109, 469). By cryoscopic investigation of equimolecular mixtures of pyridine with phenol, and of pyridine with *o*-cresol in solution in benzene or naphthalene, it is found that the compounds are considerably dissociated, the degree of dissociation increasing rapidly on dilution. Attempts are made to calculate the limits for this dissociation, taking into account the association of the compound and of its constituents.

D. F. T.

Ketens. XXIX. Comparison of Carbimides with Ketens.

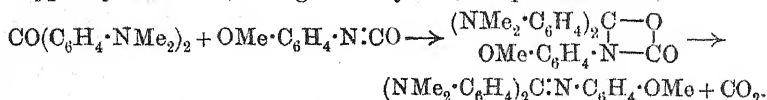
H. STAUDINGER and R. ENDLE (Ber., 1917, 50, 1042—1046).—Judging from their similarity in structure, ketens ($R\cdot CH:CO$ and $R_2C:CO$) and carbimides ($R\cdot N:CO$) should have certain reactions in common. For example, carbimides might be expected to unite with reactive unsaturated compounds to form derivatives of four-membered ring systems, which is a reaction given by ketens, especially those of the second type. Whilst they do not form such products at low temperatures, they do react at higher temperatures to give substances which can be interpreted as being degradation products of the additive compounds.

Phenylcarbimide reacts with *p*-dimethylaminobenzaldehyde at 190° to form *p*-dimethylaminobenzylideneaniline, thus:



With tetramethyldiaminothiobenzophenone at 170°, it yields phenylauramine and carbon oxysulphide, and with nitrosobenzene at 120° it forms azobenzene.

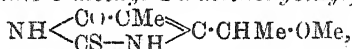
p-Methoxyphenylcarbimide and Michler's ketone yield *p*-methoxyphenylauramine, orange-red crystals, m. p. 172—173°, thus:



p-Dimethylaminophenylcarbimide might be expected to be more reactive than phenylcarbimide, but it is less so. It is obtained as follows: methyl *p*-dimethylaminobenzoate is converted into *p*-dimethylaminobenzhydrazide, m. p. 170—171°, this into the

azide, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{N}_3$, decomp. 97° , and this by heating into *p*-dimethylamino-phenylcarbimide, m. p. 39° , b. p. $90\text{--}92^\circ$ /abs. vac. The compound reacts with water to form tetramethyldiaminodiphenylcarbamide; with methyl alcohol it gives *p*-dimethylaminophenylurethane [*methyl p*-dimethylaminophenylcarbamate], m. p. $101\text{--}103^\circ$, and with aniline it yields *p*-dimethylaminodiphenylcarbamide, m. p. $207\text{--}208^\circ$. J. C. W.

Pyrimidines. LXXXV. Synthesis of a Secondary Nucleoside of Thymine and its Conversion into a Derivative of Glyoxaline by Hydrolysis with Acids. TREAT B. JOHNSON and SIDNEY E. HADLEY (*J. Amer. Chem. Soc.*, 1917, **39**, 1919—1927. Compare A., 1916, i, 754).—Ethyl β -keto- γ -ethoxy- α -methyl-*n*-valerate, $\text{OEt} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$, in the presence of alcoholic sodium ethoxide undergoes condensation with thiocarbamide, with formation of 6-*oxy*-2-*thio*-5-methyl-4- α -ethoxyethylpyrimidine, $\text{NH} \langle \begin{smallmatrix} \text{CO} \cdot \text{CMe} \\ \text{CS} \text{--} \text{NH} \end{smallmatrix} \rangle \text{C} \cdot \text{CHMe} \cdot \text{OEt}$, colourless prisms, m. p. 222° , which reacts with ethyl chloroacetate and alcoholic sodium ethoxide, with formation of ethyl 6-*oxy*-5-methyl-4- α -ethoxyethylpyrimidine-2-thioacetate, $\text{NH} \langle \begin{smallmatrix} \text{CO} \text{-----} \text{CMe} \\ \text{C}(\text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}) \text{:N} \end{smallmatrix} \rangle \text{C} \cdot \text{CHMe} \cdot \text{OEt}$, colourless prisms, m. p. 119° , and on treatment with aqueous chloroacetic acid suffers elimination of sulphur, with production of 2:6-dioxy-5-methyl-4- α -ethoxyethylpyrimidine, $\text{NH} \langle \begin{smallmatrix} \text{CO} \cdot \text{CMe} \\ \text{CO} \text{--} \text{NH} \end{smallmatrix} \rangle \text{C} \cdot \text{CHMe} \cdot \text{OEt}$, prisms, m. p. 176° . By a similar series of changes, starting with thiocarbamide and ethyl β -keto- γ -methoxy- α -methyl-*n*-valerate, there is obtained 6-*oxy*-2-*thio*-5-methyl-4- α -methoxyethylpyrimidine,



which can be further converted into 2:6-dioxy-5-methyl-4- α -methoxyethylpyrimidine, $\text{NH} \langle \begin{smallmatrix} \text{CO} \cdot \text{CMe} \\ \text{CO} \text{--} \text{NH} \end{smallmatrix} \rangle \text{C} \cdot \text{CHMe} \cdot \text{OMe}$, prisms, m. p. 217° . On heating the dioxyethoxyethyl- or dioxymethoxyethylpyrimidine compound with hydrochloric or hydrobromic acid, decomposition is effected, with formation of methylethylglyoxalone, $\begin{smallmatrix} \text{CMe} \cdot \text{NH} \\ \parallel \\ \text{CE} \text{--} \text{NH} \end{smallmatrix} \rangle \text{CO}$, but with dioxymethylethoxyethylpyrimidine, using special precautions, a small quantity of the *thymine-nucleoside*, $\text{NH} \langle \begin{smallmatrix} \text{CO} \cdot \text{CMe} \\ \text{CO} \text{--} \text{NH} \end{smallmatrix} \rangle \text{C} \cdot \text{CHMe} \cdot \text{OH}$, m. p. $219\text{--}220^\circ$, is obtained; this is extremely unstable in the presence of hot acids and readily changes into the glyoxalone compound. D. F. T.

Acid Additive Compounds of Azobenzene-*p*-hydrazones. J. TRÖGER and J. PIOTROWSKI (*Arch. Pharm.*, 1917, **255**, 233—261).—The reaction between aromatic aldehydes and azobenzene-*p*-hydrazinesulphonic acids to form hydrazones having well-marked basic properties (Tröger and Müller, A., 1908, i, 1025;

Tröger and Puttkammer, A., 1909, i, 68, 69) has been extended to aliphatic aldehydes and ketones. The condensation proceeds even more easily in these cases, but the hydrazones are sometimes difficult to isolate on account of the solubility of the salts.

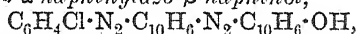
Equal molecular quantities of acetone and azobenzene-*p*-hydrazinesulphonic acid suspended in alcohol yield *isopropylideneazobenzene-p-hydrazone sulphate*, $\text{N}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_2\cdot\text{H}_2\text{SO}_4$, bluish-violet, crystalline powder, by warming with a drop of concentrated sulphuric acid on the water-bath for about fifteen minutes; the free *hydrazone*, $\text{C}_{15}\text{H}_{16}\text{N}_4$, obtained by means of 5% aqueous ammonia, forms dark brown needles, m. p. $111\cdot5^\circ$. By a similar reaction in glacial acetic acid, acetylacetone and azobenzene-*p*-hydrazinesulphonic acid (2 mols.) yield the *sulphate*, violet-brown, crystalline powder, of *acetylacetonebisazobenzene-p-hydrazone*, $\text{CH}_2(\text{CMe}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph})_2$, orange leaflets, m. p. 87° .

Azobenzene-*p*-hydrazinesulphonic acid and ethyl acetoacetate react in alcoholic hydrochloric acid, initially at 0° and finally on the water-bath, to form a mixture of a hydrochloride and a sulphate, from which 5% aqueous ammonia liberates the expected *hydrazone*, $\text{N}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, reddish-brown needles, m. p. 127° ; the *hydrochloride*, $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_4\cdot\text{HCl}$, is a violet, crystalline powder. Chloroacetaldehyde hydrate and azobenzene-*p*-hydrazinesulphonic acid yield *chloroethylideneazobenzene-p-hydrazone sulphate*, $\text{CH}_2\text{Cl}\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}\cdot\text{H}_2\text{SO}_4$, amorphous, black powder with green reflex, from which 5% aqueous ammonia liberates, not the hydrazone, but a *substance*, dark brown prisms, m. p. 200° . Dextrose and azobenzene-*p*-hydrazinesulphonic acid yield a *hydrochloride*, $\text{C}_{18}\text{H}_{22}\text{O}_5\text{N}_4\cdot\text{HCl}$, steel-blue prisms, but the free hydrazone could not be isolated.

In addition to many already recorded (*loc. cit.*), the following salts are described: *benzylideneazobenzene-p-hydrazone hydriodide*, $\text{CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}\cdot\text{HI}$, blackish-violet, amorphous powder; *p-tolylideneazobenzene-p-hydrazone sulphate*, violet needles, and *hydrobromide*, dark violet powder; *p-isopropylbenzylideneazobenzene-p-hydrazone sulphate*, ultramarine needles; *cinnamylideneazobenzene-p-hydrazone hydrochloride* and *hydrobromide*, both black, crystalline powders; *o-chlorobenzylideneazobenzene-p-hydrazone*, brownish-red crystals, m. p. $150\cdot5^\circ$, and its *sulphate*, dirty violet, amorphous powder, *hydrochloride*, brownish-violet powder, and *hydrobromide*, microcrystalline, brownish-black powder; *p-chlorobenzylideneazobenzene-p-hydrazone*, golden-yellow leaflets, m. p. 177° , and its *sulphate*, ultramarine crystals; *o-nitrobenzylideneazobenzene-p-hydrazone*, reddish-brown needles, m. p. 194° (from a little benzene), or brownish-black needles, m. p. 196° (from much benzene), and its *sulphate*, ultramarine needles, *hydrochloride*, greyish-violet needles, and *hydriodide*, brownish-black needles; *p-nitrobenzylideneazobenzene-p-hydrazone sulphate*, steel-blue needles; *salicylideneazobenzene-p-hydrazone hydrochloride*, moss-green needles, and *hydriodide*, olive-green, micro-

crystalline powder; *p*-methoxybenzylidenediazobenzene-*p*-hydrazone hydrochloride, bluish-black needles; furfurylidenediazobenzene-*p*-hydrazone sulphate, steel-blue, microscopic needles, hydrochloride and hydrobromide, blackish-violet, amorphous powders. C. S.

***p*-Chlorobenzeneazo- α -naphthylhydrazinesulphonic Acid.** J. TRÜGER and J. PIOTROWSKI (*Arch. Pharm.*, 1917, 255, 157—171).—*p*-Chlorobenzeneazo- α -naphthylamine cannot be diazotised satisfactorily by any of the usual methods. The following method gives good results under the conditions stated. An emulsion of *p*-chlorobenzeneazo- α -naphthylamine and water (30 parts) is treated with 25% hydrochloric acid (10 mols.) and warmed at about 75° for a short time until the hydrochloride has been formed. The mixture is transferred to a pressure bottle, cooled to about 45°, powdered sodium nitrite (about 2 mols.) is added, the bottle is closed and shaken two or three times, not too violently, and the liquid is at once filtered rapidly, the process of diazotisation requiring only a few seconds. The bottle should be only partly filled, and only small quantities of material (6 grams) should be operated on. The *diazonium chloride*, $C_{16}H_{10}N_4Cl_2$, which separates from the filtrate in cherry-brown or brownish-red needles, is not explosive, and can be recrystallised from hot water, but the solid appears to lose nitrogen by prolonged keeping. It couples with β -naphthol in dilute aqueous sodium hydroxide to form *p*-chlorobenzeneazo- α -naphthylazo- β -naphthol,



stellate, violet crystals with olive-green reflex, m. p. 261°, and with aniline in aqueous solution to form *p*-chlorobenzeneazo- α -naphthylazobenzene, $C_{22}H_{16}N_4Cl$, brown prisms or needles, m. p. 142°, and is converted by an alkaline solution of potassium sulphite into the metastable form of *potassium p*-chlorobenzeneazo- α -naphthyl-diazosulphonate, $C_6H_4Cl \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot SO_3K$, pale brown flocks, which changes to the amorphous, coffee-brown, stable salt by keeping for a day in the mother liquor. The last-mentioned salt is reduced by ammonium sulphide (compare Tröger and Westerkamp, A., 1910, i, 207) to *potassium p*-chlorobenzeneazo- α -naphthylhydrazinesulphonate, $C_6H_4Cl \cdot N_2 \cdot C_{10}H_6 \cdot NH \cdot NH \cdot SO_3K$, golden leaflets. The free *hydrazinesulphonic acid*, $C_{16}H_{13}O_3N_4ClS$, is a brownish-violet powder with olive-green reflex, which reacts in the presence of alcoholic hydrogen chloride with cinnamaldehyde and with salicylaldehyde to form *cinnamylidene-p*-chlorobenzeneazo- α -naphthylhydrazone, $C_{26}H_{18}ClN_2 \cdot NH \cdot N : CH : CH : CHPh$, deep cherry-red, stellate needles, m. p. 166° (decomp.), and *salicylidene-p*-chlorobenzeneazo- α -naphthylhydrazone, $C_{23}H_{17}ON_4Cl$, brown needles, m. p. 162° (decomp.), respectively.

The hydrazinesulphonic acid is reduced by zinc dust and 30% acetic acid, yielding ammonia, sulphuric acid, and *p*-chloroaniline, but the expected naphthylenediamine could not be detected.

C. S.

Structure of Yeast-nucleic Acid. P. A. LEVENE (*J. Biol. Chem.*, 1917, **31**, 591—598. Compare Jones and Read, this vol., i, 233).—The *brucine* salt of cytosine-uracil-dinucleotide melts at 200° (corr.), and, when treated with ammonia to remove the brucine and then with barium hydroxide, yields the *barium* salt of the same dinucleotide, $C_{18}H_{21}O_{16}N_5P_2Ba_2 \cdot 2H_2O$, $[\alpha]_D^{25}$, in 2.5% hydrochloric acid solution, +12.5°.

The author directs attention to the possibility of the existence of six ways of linking between two nucleotides instead of only two, as hitherto assumed (*loc. cit.*). H. W. B.

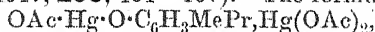
Digestibility of Starches from various Vegetable Foods by the Diastases from Malt, Pancreas, and Saliva. MARIUS PAULETIG (*Zeitsch. physiol. Chem.*, 1917, **100**, 74—92).—The author incubates solutions of the various starches with diastases from different sources, and, after two hours, notes the behaviour of the mixtures to iodine and Fehling's solutions. The chief conclusion drawn by the author is that diastase hydrolyses starch from cereals more readily than starch from the leguminosæ. H. W. B.

Action and Occurrence of Arginase. S. EDLBACHER (*Zeitsch. physiol. Chem.*, 1917, **100**, 111—116).—The activity of arginase is increased in the presence of phosphates and inhibited by soluble calcium and magnesium salts.

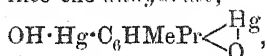
Arginase is present in the human foetal liver, but not in the kidney or small intestine. It could not be detected in yeast or in soya beans.

The specificity of arginase is illustrated by the fact that it does not liberate carbamide from either guanidinoacetic or guanidinopropionic acids. H. W. B.

Constitution of Hydrargyrum thymolo-aceticum. E. RUPP (*Arch. Pharm.*, 1917, **255**, 191—197).—The formula



which has long been given to thymol-mercuric acetate, must certainly be incorrect, since the compound does not contain ionisable mercury. It is now found that the substance is 2:6-diacetatomercurithymol, $OH \cdot C_6HMePr(Hg \cdot OAc)_2$, since its mixture with glacial acetic acid and potassium nitrate is converted by sulphuric acid in the cold into 2:6-dinitrothymol. It is converted by hot 10% sodium hydroxide into the sodium derivative of 2:6-dihydroxymercurithymol, $C_{10}H_{13}O_3NaHg_2 \cdot 3H_2O$, colourless plates, an aqueous solution of which is converted into the *anhydride*,



by carbon dioxide, into 2:6-dichloromercurithymol, colourless crystals, by a saturated solution of sodium chloride, and into 2:6-dinitratomercurithymol, colourless crystals, by 5% nitric acid. 2:6-Diiodomercurithymol has also been prepared.

The mercury in organic substances can be estimated by heating

0.3 gram of the substance with 5 c.c. of sulphuric acid and 1 gram of potassium nitrate, boiling the solution for ten to thirty minutes until it is colourless, cooling, adding permanganate until a permanent pink coloration is obtained, and, after the addition of a drop of hydrogen peroxide, titrating with $N/10$ -thiocyanate with iron alum as indicator.

C. S.

Physiological Chemistry.

Capacity of Blood and Hæmoglobin to Unite with Carbon Dioxide. G. A. BUCKMASTER (*J. Physiol.*, 1917, 51, 164—175).—Dialysed blood corpuscles have the power of absorbing carbon dioxide, and the author attributes this power to the hæmoglobin, since no other protein appears to be able to absorb carbon dioxide to the same degree.

G. B.

Tables for Finding the Alkaline Reserve of Blood Serum, in Health and in Acidosis, from the Total Carbon Dioxide or the Alveolar Carbon Dioxide or the Hydrogen-ion Concentration at Known Carbon Dioxide Tension. J. F. MCCLENDON, A. SHEDLOV, and W. THOMSON (*J. Biol. Chem.*, 1917, 31, 519—525. Compare McClendon, this vol., ii, 423).—Diagrams are given in the text by means of which it is possible to ascertain directly the alkaline reserve of the serum of the blood when the carbon dioxide or hydrogen-ion concentration of the serum under defined conditions has been estimated. The 'alkaline reserve' is defined by the authors as the difference between the sum of the equivalents of strong bases and the sum of the equivalents of strong acids in the serum, expressed as a fraction of a normal solution (compare Van Slyke and Cullen, this vol., i, 521).

H. W. B.

Influence of Respiration on the Exchange of SO_4 between Corpuscles and Plasma, and its Effect on the Excretion of SO_4 . S. DE BOER (*J. Physiol.*, 1917, 51, 211—220).—A quantity of carbon dioxide, passed into blood within physiological limits (15—20 vols. per cent.) causes SO_4 to leave the serum and to pass into the corpuscles, in which it is transported to the kidneys for excretion. Estimations of SO_4 in serum were carried out by measuring the height of the column of barium sulphate (after centrifuging in a hæmocrite) obtained from the ultra-filtrate. Normal serum contains 0.0212% SO_4 .

G. B.

The Chemistry and Physiology of the Coagulation of the Blood. III. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1917, 82, 289—309. Compare A., 1916, i, 613).—The following processes are assumed to take place in coagulation: (1) Prothrombin \rightarrow thrombin in the presence of calcium chloride, the

reaction (proteolysis) being accelerated by "activators." (2) Thrombin + fibrinogen = fibrin. Reasons are given for believing that the prothrombin is not a definite protein, neither is it derived from any particular species of blood cells. It is probably derived from various cells, and is found in the plasma in the form of higher degradation products of proteins. Experiments are described which tend to show that lipoids are not absolutely essential for the formation of thrombin from prothrombin, but that other substances can act as "activators" (accelerating proteolysis). The same remark applies to the higher fatty acids. The change into the so-called "metathrombin" (an inactive thrombin) is ascribed to an adsorption by the colloids of the serum. S. B. S.

Carbon Dioxide and the Coagulation of Blood. MARIO CHIO (Arch. Farm. speriment., 1917, 23, 202—224, 225—235; from Chem. Zentr., 1917, ii, 62—63).—Three factors have previously been recognised as necessary for the coagulation of blood: (1) fibrinogen, which yields fibrin by the action of the fibrin enzyme; (2) a pro-enzyme; and (3) soluble and ionised salts of calcium which, by union with the pro-enzyme, yield the fibrin enzyme. According to the author's experiments on the plasma of rabbits and guinea-pigs, a fourth factor must be taken into account, namely, carbon dioxide, on the tension of which the equilibrium of the calcium salts, and consequently the possibility of their union with the pro-enzyme to enzyme, depends. The author considers that the difference in behaviour of blood withdrawn from the organism and blood in the body is caused by the former not being enclosed in a vessel made of living tissue and by being in contact with gases at a different tension. Efforts to provide a suitable substitute for the living tissue were unsuccessful. On the other hand, it was found possible to collect the blood in a vessel containing a mixture of oxygen and carbon dioxide in which the partial pressure of the latter could be maintained within the physiological limits (30—50 mm. mercury). A distinct change in the conditions of coagulation was then observed. Whilst, otherwise, blood coagulated within a few minutes in ordinary or paraffined glass vessels, guinea-pig blood was not completely coagulated within an hour in a paraffined vessel in an atmosphere of carbon dioxide (2 vols.) and oxygen (1 vol.) at a pressure of 50 mm. (partial pressure of carbon dioxide, 33.3 mm.), and rabbit's blood remained liquid after this period and was not entirely coagulated after four hours; even in ordinary glass vessels, coagulation did not commence in the latter case until after twenty-five minutes. After addition of salt, the plasma of either animal refused to coagulate in an atmosphere of carbon dioxide at 20—30 mm. pressure. It did not, however, lose its ability to coagulate, but the fibrin enzyme completely lost its activity, probably because it is a product of a balanced action in which carbon dioxide is one factor affecting the equilibrium. Calcium salts and carbon dioxide are mutually antagonistic.

H. W.

Metabolism of Arginine. III. Arginine and Creatine Formation. W. H. THOMPSON (*J. Physiol.*, 1917, **51**, 111—153).—A daily dose of 2 grams of arginine carbonate given to dogs by the mouth increases the creatine output by 10%, but this represents only a methylation of 2.5% of the guanidine nucleus given. In ducks, these figures are 22.6% and 1.1% respectively. When arginine is injected hypodermically, more (about twice as much) creatine is formed, than after administration by the mouth. After intravenous injection of arginine in rabbits, some creatine formed from it (8—25% of the guanidine nucleus) is stored in the muscles, at least temporarily, and some is at once excreted in the urine (about 1% during the first three hours after injection). The percentage figures for the excretion of arginine in dog's urine as total nitrogen, urea, ammonia, amino-acid, and total creatinine nitrogen are: for feeding, 56.5, 34.7, 13.7, 2.33, and 3.47 respectively, and for hypodermic injection, 67.87, 35.4, 4.05, 4.7, and 4.12 respectively.

G. B.

Nutritive Value of Margarines and Butter Substitutes with Reference to their Content of the Fat-soluble Accessory Growth Substance. W. D. HALLIBURTON and J. C. DRUMMOND (*J. Physiol.*, 1917, **51**, 235—251).—The fat-soluble accessory growth substance of beef-fat and "oleo-oil" is present in margarines prepared on such a basis. Such margarines are nutritively equivalent to butter. Coconut oil, cotton-seed oil, Arachis oil, and hydrogenated vegetable oils contain little or none of this accessory substance. Margarines from these, and nut butters prepared from crushed nuts, are not equal to butter in nutritive value. Lard substitutes from vegetable oils are equal to lard in nutritive value, both alike being destitute of the fat-soluble accessory substance.

G. B.

Growth. IX. Influence of Tethelin on the Early Growth of the White Mouse. T. BRAILSFORD ROBERTSON and M. DELPRAT (*J. Biol. Chem.*, 1917, **31**, 567—574. Compare Robertson, A., 1916, i, 350).—The administration of tethelin (a lipid extracted from the anterior lobe of the pituitary gland) to female mice does not have any appreciable effect on the growth of the suckling young. After the fourteenth day, when the eyes of the young mice are open and they have access to food other than that supplied to the mother, the administration of tethelin to the young animals results in a noticeable acceleration of growth during the second growth cycle (second to fifth weeks), which is followed by a marked retardation during the subsequent third growth cycle, even though the administration of tethelin is discontinued at the end of the fifth week.

H. W. B.

Synthetic Sugar Formation in the Artificially Perfused Liver. II. KARL BALDES and FRITZ SILBERSTEIN (*Zeitsch. physiol. Chem.*, 1917, **100**, 34—53. Compare Embden, Schmitz, and Wittenberg, A., 1913, i, 1411).—The results of perfusion experiments

on the livers of phloridzinised dogs indicate that lactic acid is converted into dextrose with the intermediate formation of glyceraldehyde. The addition of glyceric or pyruvic acid or of glycollaldehyde to the perfusing fluid did not lead in any case to the formation of dextrose.

H. W. B.

Factors Necessary for the Formation of Carbamide from Ammonia and Carbon Dioxide in the Isolated Liver. I. Behaviour of Ammonium Carbonate Circulated with Ringer's Solution through the Isolated Liver. ANTONIO CLEMENTI (*Arch. Farm. speriment.*, 1917, **33**, 289—304; from *Chem. Zentr.*, 1917, ii, 173—174).—It has been previously observed by Schröder that carbamide is formed when a solution of ammonium carbonate in defibrinated blood is circulated through the isolated liver; such formation does not occur when the defibrinated blood is replaced by Ringer's solution. In experiments with the liver of the dog, small quantities of carbamide were detected when ammonium carbonate was not added; after addition of this substance the amount of carbamide was only very slightly increased, and this result is probably attributable to a further action of liver arginase. The added ammonia is almost quantitatively recovered, partly from the solution and partly from the liver tissue. One or more components of defibrinated blood must therefore be necessary for the formation of carbamide.

H. W.

Glycolytic Properties of Muscular Tissue. RALPH HOAGLAND and C. M. MANSFIELD (*J. Biol. Chem.*, 1917, **31**, 501—517).—When pieces of muscular tissue from the ox, freed from blood by draining, but not by washing out the vessels with water or saline solution, are incubated under strictly aseptic conditions, a disappearance of dextrose occurs without the production of an equivalent amount of carbon dioxide. The glycolysis takes place most rapidly during the first few hours after the death of the animal and then progresses at a slow rate for several days. In some cases a preliminary increase in the total carbohydrate is observed owing to the production of glycogen, which appears to indicate the existence of a capacity for synthesis as well as for catalysis of dextrose by the tissue enzymes. The formation of disaccharides was not detected (compare Levene and Meyer, A., 1912, ii, 577).

H. W. B.

Chemistry of Lactacidogen. II. GUSTAV EMBDEN and FRITZ LAQUER (*Zeitsch. physiol. Chem.*, 1917, **100**, 181. Compare A., 1915, i, 345).—By treating an extract of muscle containing lactacidogen with phenylhydrazine, the crystalline phenylhydrazine salt of the phenylosazone of hexosephosphoric acid is obtained. Lactacidogen must therefore possess a structure similar to that of hexosephosphoric acid.

H. W. B.

Function of Muscular Tissue in Urea Formation. RALPH HOAGLAND and C. M. MANSFIELD (*J. Biol. Chem.*, 1917, **31**,

487—499).—The amount of urea in muscular tissue does not alter during aseptic autolysis, indicating the absence of urease and of urea-forming enzymes, such as arginase. H. W. B.

[Selenium in Bones, Teeth, and Urine]. TH. GASSMANN (*Zeitsch. physiol. Chem.*, 1917, 100, 182—189).—See this vol., ii, 540.

Specific Pigment-forming Ferment of the Skin, Dopaoxydase. BR. BLOCH (*Zeitsch. physiol. Chem.*, 1917, 100, 226—254).

—When a frozen section of human or other skin is treated with a 1% solution of 3:4-dihydroxyphenylalanine (termed “dopa”), oxidation and condensation occur with the formation of a dark brown or black pigment (*dopamelanin*) at certain definite places owing to the action of an intracellular oxidising enzyme, *dopaoxydase*. The oxydase is present in the protoplasm (not the nuclei) of the basal cells of the epidermis and the cells of the hair follicles, and is of a highly specific nature, exerting no action on tyrosine, quinol, homogentisic acid, pyrogallol, tryptophan, adrenaline, and other substances more or less closely related to 3:4-dihydroxyphenylalanine. A parallelism is observed between the pigmentary changes occurring in sections of skin under the action of chemically active light rays and those immersed in “dopa,” and the conclusion is drawn that the natural pigment is probably formed in the living organism from 3:4-dihydroxyphenylalanine or a substance very similar to it in chemical constitution.

Dopaoxydase is destroyed on heating to 100°. Water, physiological salt solution, half-saturated ammonium sulphate solution, alcohol, acids, and alkalis also inactivate the enzyme; fat solvents, such as ether and benzene, do not destroy its activity. Poisons, such as prussic acid, toluene, formaldehyde, etc., also destroy the enzyme.

The action of dopaoxydase was tested, with negative results, on the following new substances. *α -Amino- β -4-hydroxy-3-methoxyphenylpropionic acid*, $C_{10}H_{13}O_4N$, is prepared by condensation of vanillin with hippuric acid, reduction of the resulting *α -benzoyl-amino- β -4-hydroxy-3-methoxycinnamic acid*, and subsequent elimination of the benzoyl radicle by heating with hydrochloric acid under a reflux condenser. The substance goes brown at 240° and melts at 256° (decomp.). It yields a momentary blue colour with a drop of ferric chloride, which then turns green and finally becomes colourless. *α -Amino-4-hydroxy-3-methoxyphenylacetic acid*, $C_9H_{11}O_4N$, is obtained by shaking vanillin in ethereal solution with potassium cyanide solution in the presence of ammonium chloride and proceeding in a manner similar to that described by Fromberg and Hermanns (A., 1914, i, 905) for the preparation of *α -amino-4-hydroxyphenylacetic acid*. It crystallises in white, silky needles, m. p. 240° (decomp.), and gives a momentary, olive-green colour with a drop of ferric chloride solution. On treatment with hydriodic acid the substance yields *α -amino- β -3:4-dihydroxyphenylacetic acid*, $C_8H_9O_4N$, white, crystalline powder, which gives a dark green colour with ferric chloride solution, turning intense purplish-red on the addition of sodium hydroxide. H. W. B.

Production of Creatinuria in Normal Adults. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1917, **31**, 561—566. Compare Denis, Kramer, and Minot, this vol., i, 526).—Feeding two normal women with a high protein (creatine-free) diet causes creatinuria, which disappears when the amount of protein in the diet is reduced. Similar experiments on two men invariably yielded negative results, although the amount of protein consumed was sufficient to raise the nitrogen eliminated in the urine to 34.5 grams daily. H. W. B.

Formation of Thiocyanic Acid in Animals. SERAFINO DEZANI (*Arch. Farm. speriment.*, 1917, **23**, 245—256; from *Chem. Zentr.*, 1917, ii, 178).—The decomposition of the nitriles of fatty acids in the animal organism occurs, according to Lang (*Arch. exp. Path. Pharm.*, **36**, 75), in such a manner that the cyano-group is eliminated and converted into thiocyanic acid, and the residue is completely oxidised; four-fifths to five-sixths of the acid is destroyed, whilst one-sixth to one-fifth appears in the urine. The hypothesis has been the subject of some criticism. The author has therefore estimated the ratio of acid sulphur to neutral sulphur in the urine of dogs to which acetonitrile had been administered. If Lang's hypothesis is correct, an increase in neutral sulphur, but also a much greater increase in acid sulphur, is to be expected, and consequently an increase in the above ratio. The amount of thiocyanic acid in the urine was smaller than that indicated by Lang and did not exceed one-tenth of that theoretically derivable from the administered nitrile. The presence of acetic acid in the urine could not be detected. With large and small doses of nitrile (in quantity insufficient to produce poisoning), the ratio of the two forms of sulphur diminished. With big doses, the total sulphur was decreased, the acid sulphur greatly increased, and the neutral sulphur almost unchanged. With small doses, the total sulphur was slightly increased, the effect being due to increase in the neutral sulphur. The author is therefore drawn to the conclusion that all the thiocyanic acid formed appears as such in the urine, and that the decomposition of the nitrile only occurs to a small extent in this sense; the greater bulk is probably hydrolysed and the acetic acid produced is completely oxidised in the organism.

The formation of thiocyanic acid after administration of nitriles has previously been observed only with mammals; the author finds it also to take place with fowls, but only in small quantity and after administration of large doses of nitriles. The greater resistance of birds to nitriles is confirmed. H. W.

Inhibition of Enzymic Reactions by Urine. HANS EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1917, **100**, 202—225).—Normal and pathological urines contain a substance which strongly inhibits the enzyme action of invertase, catalase, and diastase. The substance is not destroyed by boiling the urine and is not adsorbed by animal charcoal. It does not appear to be urea or uric acid, neither is it a substance derived from the bile, because

it is insoluble in chloroform, and extracts of gall-stones do not exert any similar inhibitory action on the enzymes studied. The substance does not readily dialyse through parchment, which suggests that it is of colloidal nature in spite of its behaviour towards animal charcoal and heat.

The inhibitory substance occurs in very variable amounts in pathological as well as in healthy urines, and doubtless influences the actions of the enzymes which may be present. In diabetes, for instance, the low diastatic power of the urine (compare Wohlgemuth, A., 1909, ii, 1037) may be due either to a small amount of enzyme or to a large proportion of inhibitory substance accompanying a normal quantity of enzyme. H. W. B.

Toxicity of Phosphates in Relation to the Calcium in the Blood and to Tetanus. CARL BINGER (*J. Pharm. Exper. Ther.*, 1917, 10, 105—120).—Solutions of phosphoric acid and its sodium salts, when injected intravenously into dogs, cause a diminution in the amount of calcium in the serum proportionate to the amount of phosphate introduced. When a dihydrogen phosphate is injected in an amount equivalent to 150 mg. of phosphorus per kilo. of body-weight, the calcium in the serum becomes reduced from 10 mg. to approximately 6 mg. per 100 c.c. of serum. After the injection of a di- or tri-alkali phosphate, a similar reduction in the calcium content of the serum is observed, but it is accompanied by typical symptoms of tetanus. The mechanism of the production of tetanus in these circumstances has not been elucidated (compare Greenwald, A., 1915, i, 1037). H. W. B.

Origin of Creatine. II. L. BAUMANN and H. M. HINES (*J. Biol. Chem.*, 1917, 31, 549—559).—Incubation of minced animal tissues with glycocyamine does not lead to the production of creatine, but after the injection of glycocyamine into rabbits and dogs, an increased excretion of creatine is sometimes observed. The formation of creatine in the animal organism from arginine may therefore occur, with the intermediate formation of glycocyamine (compare Mellanby, A., 1908, ii, 308). H. W. B.

Comparative Investigation of the Behaviour of Hydroaromatic Substances in the Animal Organism. Y. SASAKI (*Acta Schol. Med. Kyoto*, 1917, 1, 413—423; from *Physiol. Abstr.*, 1917, 2, 344).—Cyclohexanol and 1:4-dihydroxycyclohexane given by the mouth to rabbits, caused an increased output of ethereal sulphates and the appearance of glycuronic acid in the urine. Phloroglucinol, and *i*-inositol (cyclohexane derivatives with three and with six hydroxyl groups respectively) did not do this, except that a single very large dose of phloroglucinol increased the output of ethereal sulphates in the dog. Toxicity tests on mice show that an increase in the number of hydroxyl groups decreases the toxicity. These substances are, in their biological behaviour, a link between the aliphatic alcohols and the aromatic phenols. G. B.

Toxic Action of Opium Alkaloids Individually and in Combination with each other on Paramæcia. DAVID I. MACHT and HOMER G. FISHER (*J. Pharm. Exper. Ther.*, 1917, 10, 95—104).—Members of the papaverine group of alkaloids are very toxic towards *Paramæcium putrinum*, whereas members of the morphine group are comparatively innocuous. The toxic effect of a combination of two or more members of the same group of alkaloids is the sum of the toxic effects produced by each alkaloid separately. Combinations of members of different groups produce a synergistic effect, that is, the resultant effect is greater than the sum of the individual toxicities. It is probable that the toxicity of papaverine and other related alkaloids is associated with the benzyl group present in the molecule.

Papaverine, dionine, and, to a lesser degree, narcotine and narceine, exert a narcotic or anæsthetic action on paramæcia which is distinct from the toxic action.

H. W. B.

Intermediate Metabolism in Experimental Phosphorus Poisoning. S. ISAAC (*Zeitsch. physiol. Chem.*, 1917, 100, 1—33. Compare Frank and Isaac, A., 1911, ii, 315).—Perfusion experiments with the livers of dogs taken in the later stages of phosphorus poisoning show that under these conditions the normal transformation of lactic acid into dextrose and glycogen does not occur (compare Parnas and Baer, A., 1912, ii, 778). The primary degradation of saturated to unsaturated fats also appears to be inhibited, although the subsequent oxidation of the lower fatty acids occurs as in the normal animal. Phosphorus poisoning is not accompanied by any sign of lessened oxidation in the liver (compare Isaac and Loeb, following abstract).

H. W. B.

Respiratory Metabolism of the Artificially Perfused Livers from Dogs after Phosphorus Poisoning. S. ISAAC and A. LOEB (*Zeitsch. physiol. Chem.*, 1917, 100, 54—58).—In severe cases of phosphorus poisoning, the oxygen consumption per kilogram of liver tissue per minute during perfusion was found to fall within the limits obtained for livers from normal animals. Phosphorus poisoning is not accompanied, therefore, by diminished oxidative processes in the liver (compare Isaac, preceding abstract).

H. W. B.

Volatility of Organic Compounds as an Index of the Toxicity of their Vapours to Insects. WILLIAM MOORE (*J. Agric. Research*, 1917, 10, 365—371).—The work done on the benzene derivatives (compare this vol., i, 527) has been extended to a large series of other compounds, those studied being hydrocarbons, esters, acids, ethers, aldehydes, ketones, alcohols, haloid and thio-derivatives, nitro-compounds, nitriles, alkaloids, pyridine, and terpenes. In general, decreasing volatility is accompanied by an increase in toxicity. Compounds with boiling points of 225—250° and upwards are usually so slightly volatile that they

do not produce death in the case of the house-fly except after very long exposures. The author suggests that the structure of the respiratory system of the insect is probably responsible for the influence of volatility on the toxicity of the vapour of organic compounds.

W. G.

Chemistry of Vegetable Physiology and Agriculture.

Asymmetric Hydrolysis of Racemic Polypeptides by Killed Bacteria. I. T. MIRO (*Acta Schol. Med., Kyoto*, 1917, 1, 433—438; from *Physiol. Abstr.*, 1917, 2, 320).—The bacterial ferments of *B. coli communis* and *Staphylococcus aureus* split *DL*-leucylglycine asymmetrically; this peptide resists pancreatic ferments. The copper salt of *L*-leucine was isolated, whilst the optical activity of the mother liquor was compatible with the presence of *D*-leucylglycine.

G. B.

Asymmetric Splitting of Racemic Tyrosine by *Bacillus proteus vulgaris* and *Bacillus subtilis* (Biological Method of Preparing *D*-Tyrosine). M. TSUDJI (*Acta Schol. Med., Kyoto*, 1917, 1, 439—448; from *Physiol. Abstr.*, 1917, 2, 320).—With the former organism 65—76% of *D*-tyrosine was isolated and identified; *D*-*p*-hydroxyphenyl-lactic acid, *p*-hydroxyphenylpropionic acid, and *p*-hydroxyphenylethylamine were isolated from the decomposition products, and were derived from *L*-tyrosine. The author claims that *B. proteus* is a suitable agent for the preparation of *D*-tyrosine. With *B. subtilis* there was only a very slight degree of cleavage.

G. B.

Chemical Composition and Formation of Enzymes. XIII. Alterations in the Amount of Enzyme in Kephir Cells and in *B. lactis acidii*. H. EULER [with E. GRIESE] (*Zeitsch. physiol. Chem.*, 1917, 100, 59—68. Compare Euler and Cramér, A., 1914, i, 364).—Kephir cells which have been grown previously once or twice in a mixture of whey and galactose, with and without the addition of phosphates, contain a larger quantity of enzyme in relation to dry weight than is contained in the original material. In other words, the same weight of kephir cells produces a more rapid and a greater evolution of carbon dioxide after propagation in a suitable medium than in the original condition.

When the lactic acid bacillus is similarly grown in successive fresh quantities of a medium of whey containing 4% of galactose, the rate of formation of lactic acid by a standard number of bacilli is increased. If, however, 6% of sodium dihydrogen or disodium hydrogen phosphate is also present in the medium, the formation of the lactic acid soon diminishes, and, instead, an increasing quantity

of carbon dioxide is produced. By suitable preliminary treatment, therefore, it is possible to stimulate the production of one or other of the enzymes in the living cell.

H. W. B.

Biochemical Activity of Agglutinated Bacteria. AMILCARE ZIRONI (*Atti R. Accad. Lincei*, 1917, [v], 26, ii, 19—23).—The author's experiments on the paratyphoid bacillus *B* and the cholera vibrio show that these organisms produce the same quantity of acid and of carbon dioxide, and reduce methylene-blue to the same extent respectively, whether they are agglutinated or not.

R. V. S.

Glycolysis. GERSON G. WILENKO (*Zeitsch. physiol. Chem.*, 1917, 100, 255—263).—The fermentation of dextrose by yeast occurs without the formation of carbon dioxide when the hydroxyl-ion concentration of the medium is maintained within certain limits. This can be effected by adding a buffer-mixture of sodium dihydrogen and disodium hydrogen phosphates in the proportion of one of the former to ten or more (depending on the kind of yeast) of the latter. The same result can be achieved without phosphates by the simple addition of a slight excess of *N*-sodium hydroxide solution. If the yeast at the end of an experiment is collected and treated with fresh dextrose solution, ordinary fermentation with evolution of carbon dioxide ensues, indicating that in the original experiment the hydroxyl ions are associated with the dextrose or its degradation products rather than directly with the enzyme.

H. W. B.

Alcoholic Fermentation at Different Concentrations of Hydroxyl Ion. HANS EULER [with KNUT HALDIN] (*Zeitsch. physiol. Chem.*, 1917, 100, 69—73. Compare Wilenko, preceding abstract).—The fermentation of dextrose by yeast proceeds even in the presence of alkalinity equivalent to *N*/20-ammonium hydroxide solution. If an adequate proportion of ammonium phosphate is also added, the production of carbon dioxide is greatly diminished, although the amount of dextrose fermented may be as great as it was before the addition of the ammonium phosphate, similar conditions of time, temperature, and concentration being maintained.

H. W. B.

The Increase of Dry Weight of Yeast when Urea is Used as the Source of Nitrogen. TH. BOKORNY (*Biochem. Zeitsch.*, 1917, 82, 359—390).—A number of experiments are quoted which show that considerable growth of yeast (as measured by increase in dried weight) can take place when the organism is grown on urine containing sugar. The urea, and not hippuric acid, acts as the source of nitrogen. The growth is especially vigorous in presence of air.

S. B. S.

Saccharophosphatase of Yeasts and the Fermentation of Sucrose Phosphoric Acid. KEMAL DJENAB and CARL NEUBERG (*Biochem. Zeitsch.*, 1917, 82, 391—411).—Yeasts contain a ferment

"saccharophosphatase," which can hydrolyse the salts of synthetic sucrose phosphoric acids, prepared originally by Neuberg and Pollak (hesperonal). Scission of inorganic phosphate takes place. The ferment is found both in top and bottom yeasts. It is to be distinguished from the already known hexophosphatase in that the latter acts only in yeast juices separated from the living cell, whereas the new saccharophosphatase will act in the living cell, and produce alcoholic fermentation of the synthetic sucrose phosphate. It is also insensitive to the action of antiseptics, both when fresh yeast is used or maceration juice. It acts between the temperatures of 22° and 37°, and in neutral, alkaline, and weakly acid (acetic acid) solutions. The soluble sodium salts of the synthetic sucrose phosphoric acid can be hydrolysed to the extent of 67% by fresh yeast and 45% by maceration juice. S. B. S.

Autoregulation of the Course of Reaction in Fermentative Processes. L. LICHTWITZ (*Deut. med. Woch.*, 1917, 43, 643—646; from *Chem. Zentr.*, 1917, ii, 106).—Enzymatic processes in closed system lead to a true equilibrium or to a cessation of action, the latter state being caused by inactivation of the ferment. Natural systems of reaction are not closed, since the ultimate products are continuously removed either by subsequent processes or by separation. In natural systems, a chain of processes is always involved, in which a fixed order of velocities of reaction is always maintained (for example, the intermediate storage of sugar). This order is caused by the action of the products of fermentation on the ferment itself. The mechanism of such action is explained by an investigation of the kinetics of the inversion and fermentation of yeast. The application of these ideas is extended by investigations of the final stages of the decomposition of albumin and by consideration of protein metabolism. H. W.

Behaviour of some Organic Substances in Plants. VIII. G. CIAMICIAN and C. RAVENNA (*Gazzetta*, 1917, 47, ii, 99—107).—The experiments were conducted by watering seeds, and subsequently the growing plants, with 1% solutions of the substances investigated. In the case of maize and beans, evidence of the production of salicin was obtained when saligenin was administered. When beans are treated in the same way with benzyl alcohol, traces of a compound are formed, which yields the alcohol again when boiled with hydrochloric acid. In the same way, quinol gives rise to a compound, probably of the nature of a glucoside. R. V. S.

Relationship between Sugar Fermentation and Sugar Assimilation. TH. BOKORNY (*Allg. Brau. Hopfen-zeitung*, 1917, 57, 447—480; from *Chem. Zentr.*, 1917, ii, 23).—External factors have, without doubt, a considerable influence on this relationship. Light, which is necessary with green plants, is probably unimportant with respect to yeast, but access of air has a more marked effect. In the present communication, the influence of fractional addition of sugar, of nitrogen nutriment, and of addition of alkali

are considered. The increase in dry substance in the fermenting yeast is regarded as a criterion of the extent of assimilation. Under unfavourable conditions a loss in weight occurs, but, in better circumstances, the extent of assimilation exceeds that recorded by Pasteur, according to whom about 1% of the sugar is assimilated. Repeated addition of sugar without alteration in the total quantity appears beneficial. Carbamide, even in pure aqueous solution, is a more suitable source of nitrogen than ammonia; apparently this is more effective when gradually formed than when applied in the pre-formed state. Similarly, assimilation is favoured by the substitution of sucrose for dextrose. Assimilation is promoted by free potassium hydroxide at certain concentrations, preferably at about 0.01%. Previous experiments on the application of dextrose as a food for moulds and for the formation of starch in *Spirogyra* are discussed; in the latter instance, the influence of light and of access of oxygen is particularly noticeable. H. W.

Benzene Derivatives as Sources of Nourishment. TH. BOKORNY (*Zentr. Physiol.*, 1917, **32**, 55—63; from *Chem. Zentr.*, 1917, ii, 22).—It has been observed that the cells of certain plants (fungi, moulds, algæ) are capable of utilising derivatives of benzene for the production of albumin. Since it has been shown by Loew that quinic acid, which is frequently present in the cells of plants, can be decomposed into two molecules of propionic acid, and that the latter can be assimilated, the author puts forward the hypothesis that quinic acid is first produced in the cell from assimilable benzene derivatives and is subsequently decomposed into propionic acid and carbon dioxide. H. W.

The Physiological Significance of Potassium in Plants. JULIUS STOKLASA (*Biochem. Zeitsch.*, 1917, **82**, 310—323).—The author replies in detail to the criticisms of Weevers (this vol., i, 372).—The latter maintains that potassium is essential to the synthesis of proteins in plants, whereas the former maintains that it is essential for synthesis of carbohydrates. A large number of results already published are quoted which are stated to support the thesis of the author. S. B. S.

A New Reagent for Phloroglucinol and Catechol: the Distribution of these Substances in the Plant Kingdom. MARIANNE JOACHIMOWITZ (*Biochem. Zeitsch.*, 1917, **82**, 324—358).—*p*-Dimethylaminobenzaldehyde dissolved in sulphuric acid is a reagent for phloroglucinol, and gives a quicker and more localised reaction than Lindt's reagent. It was applied (microchemically) to the investigation of 464 different plants to determine the distribution of substances giving a coloration with it. Catechol gives the same reaction with this reagent, and macrochemical investigation reveals the fact that in many cases the coloration produced is due, at any rate partly, to this substance. S. B. S.

Wasahba Wood. G. BURTON BAKER (*Chem. News*, 1917, **116**, 139).—Wasahba wood is a very hard, almost bony wood, D 1.214,

which is sometimes used for fishing rods. The tree is supposed to be a native of British Guiana, where it attains a diameter of about 3 ft. When under the plane, the wood produces a quantity of resinous, gamboge-like dust which becomes salmon-pink with soap or alkalis. An alcoholic extract is colourless, and may be used as an indicator in the titration of ammonia and alkali hydroxides, the readings being almost the same as those obtained with phenolphthalein. An alkaline extract is a good stain for white wood.

J. C. W.

Presence of Nitrites and Ammonia in Diseased Plants.

II. Oxydases and Diastases; their Relation to the Disturbance. P. A. BONCQUET and MARY BONCQUET (*J. Amer. Chem. Soc.*, 1917, **39**, 2088—2093. Compare this vol., i, 74).—The phenomena in some plants infected by nitrate-reducing organisms seem to be co-ordinated for the preservation and increase of the nitrogen content of the plant tissues. The oxidising enzymes present appear to assist this purpose by tending to neutralise the reducing activities of the invading bacteria; the reduction in the size of secondary organs seems intended to economise the nitrogen and to preserve it for the more essential parts, such as the roots and leaves; the increased transpiration of water and the increase in the root system also are indicative of an augmented tendency to supply the plant with the necessary nitrates. The higher percentage of ash in diseased plants of this type is probably the result of these endeavours, but the fact that nevertheless a deficiency of total nitrogen is found in the tissues suggests that the reducing bacteria, in converting the nitrates into nitrites and ammonia, cause a waste of this element and induce a disease of nitrogen starvation.

D. F. T.

Symptoms of Poisoning by certain Elements, in Peltandra and other Plants. E. E. FREE (*The Johns Hopkins Univ. Circular*, 1917, 195—198 [393—396]; from *Physiol. Abstr.*, 1917, **2**, 389).—Compounds of As, Ba, Br, Co, Cu, Pb, Mn, Ni, Ag, Ur, V, and Zn gave no determinable poisonous effects in the concentrations used. Pronounced toxic effects of B, Cr, I, Li, and Hg on the leaves are described. The evidence suggests that the poisons caused injury where the transpiration of water increased the concentration of the poison locally.

G. B.

The Occurrence and Significance of Mannitol in Silage.

ARTHUR W. DOX and G. P. PLAISANCE (*J. Amer. Chem. Soc.*, 1917, **89**, 2078—2087).—In the production of maize silage, the amount of volatile acid, lactic acid, carbon dioxide, and alcohol formed is insufficient to account for the whole of the sucrose which has undergone fermentation, and the deficit is largely explained by the formation of mannitol which originates from the fructose portion of the sucrose molecule by bacterial reduction. During the fermentation of silage, the quantity of mannitol present gradu-

ally increases until approximately the twelfth day, after which a rapid decrease sets in, probably due to further bacterial alteration. The suggestion is made that mannitol could be economically extracted from silage and converted on a commercial scale into the nitrate for use as an explosive.

D. F. T.

Methods for Determining the Reaction of Soils. HARALD R. CHRISTENSEN (*Soil Sci.*, 1917, 4, 115—178).—A review is given of the various methods which have been proposed for the determination of the acidity and the lime requirement of the soil. On the basis of a considerable number of comparative experiments with Danish soils, the author suggests the necessity of distinguishing between the absolute acidity of the soil and its ability to liberate acids from neutral salt solutions (that is, to absorb bases). This distinction is, however, somewhat arbitrary, as for the former purpose the use of potassium chloride solutions is mentioned, whilst for the latter, solutions of calcium acetate are considered suitable.

These two methods were employed extensively, and the results of the tests correlated with the behaviour of the soil towards the acid test for free carbonate, the litmus, potassium iodide-iodate, and *Azotobacter* tests. The use of *p*-nitrophenol as a soil acidity indicator was also adopted.

In general, the digestion of soils with calcium acetate solution gave high positive results, even in the case of neutral and slightly alkaline soils, whilst greater correspondence was shown between the potassium chloride and the various qualitative methods. With distinctly acid soils, the ratio between the amount of acid liberated in potassium chloride and calcium acetate solutions was often below 1:10, but with neutral and slightly acid soils it frequently rose to 1:40 or more.

It is considered that in some soils part at least of the reaction is due to the presence of truly acid substances, and this agrees with the results of electrometric determinations.

A determination of the base absorption power of a soil (calcium acetate method) is not sufficient for indicating its lime requirement, nor do the results of the acidity method (with potassium chloride) give positive information on the point. It is stated, however, that all mineral soils having an acid reaction for litmus have a large lime requirement, but that many soils neutral to litmus also respond to treatment.

The lime requirement of a soil appears to be determined by the presence or absence of certain easily decomposable calcium (or magnesium) compounds capable of neutralising acids, but the question remains open as to which method will serve to indicate this need.

H. B. H.

Organic Chemistry.

Condensation of Unsaturated Systems. H. J. PRINS (*Chem. Weekblad*, 1917, 14, 932—939).—A theoretical paper, in which the author discusses the condensation of unsaturated compounds in the light of his theory of valency and affinity. A. J. W.

The Supposed Keto-enol Isomerism of Ethyl Succinylsuccinate and Ethyl *p*-Dihydroxyterephthalate. A. HANTZSCH (*Ber.*, 1917, 50, 1213—1216. Compare Gibbs and Brill, A., 1915, i, 648, and Brill, A., 1916, ii, 591).—It is claimed that Brill's evidence that the above esters exist, even in the state of solids with constant m. p.'s, as keto-enol mixtures, is based on wrong results obtained in the Meyer titration for enols (compare Hantzsch's views, A., 1915, i, 495, 551). J. C. W.

Bile Acids. III. Structural Relations between Cholic and Deoxycholic Acids. HEINRICH WIELAND and HERMANN SORGE (*Zeitsch. physiol. Chem.*, 1916, 98, 59—64).—On distillation of deoxycholic acid in a vacuum (12 mm.) at 320—340°, a heavy oil distils over and solidifies to a colourless resin, which consists of *β*-choladienecarboxylic acid, $C_{24}H_{36}O_2$. It crystallises in slender needles which, when heated, soften at 127°, m. p. 132—133°. It gives a coloration with acetic anhydride and sulphuric acid which is first red, then brown, and finally olive-green; at the same time, an intense green fluorescence is exhibited, which is also produced by the sulphuric acid alone. The substance is unsaturated and decolorises permanganate solution; it is isomeric with the choladienecarboxylic acid obtained by the reduction of cholatrienecarboxylic acid, which has been prepared by the distillation of cholic acid (Wieland and Weil, A., 1912, i, 830). Further reduction by hydrogen in the presence of palladium black converts both α - and β -choladienecarboxylic acids into the same cholanecarboxylic acid. It follows, therefore, that deoxycholic acid differs from cholic acid in having only two instead of three alcoholic hydroxyl radicles, so that these compounds may be termed the dihydroxy- and the trihydroxy-cholanecarboxylic acids respectively.

It has been shown (Wieland and Weil, *loc. cit.*) that on oxidation of cholatrienecarboxylic acid with permanganate a molecule of acetic acid is formed, which indicates the presence of a $C:CH\cdot CH_3$ group. Cholic acid itself therefore probably contains the grouping $C(OH)\cdot CH_2\cdot CH_3$ or $CH\cdot CH(OH)\cdot CH_3$. It is now shown that *β*-choladienecarboxylic acid when similarly oxidised with permanganate does not yield any acetic acid. It follows that the above hydroxyl radicle is absent in deoxycholic acid, whilst probably the remaining hydroxyl radicles occupy the same positions in each acid.

When the distillation of deoxycholic acid is carried out rapidly, a

compound is obtained which is isomeric with β -choladienecarboxylic acid. It crystallises in needles, which, when heated, soften at 204° , m. p. 215 — 217° . The new substance is not an acid, and does not give a Liebermann colour reaction. H. W. B.

Osazones from Mixtures of Formaldehyde and Starch. H. MAGGI and G. WOKER (*Ber.*, 1917, 50, 1188—1189. Compare this vol., i, 61, 447).—An osazone, m. p. 181 — 182° , crystallising in yellow rosettes, has been obtained from the dialysate of a mixture of formaldehyde and starch which had been kept at 40 — 50° for half-an-hour. The sugar may possibly be a mixture of maltose and isomaltose. It is fermentable by yeast. J. C. W.

Formaldehyde as a Hydrogenase Model, and some Observations on Formaldehyde Condensations. G. WOKER and H. MAGGI (*Ber.*, 1917, 50, 1189—1191).—Solutions of lead acetate containing formaldehyde and sulphur soon darken at 100° , and appear distinctly dark if left in the light for some days at the ordinary temperature, owing to hydrogenation of the sulphur. Lead acetate is much more soluble in "formalin" than in water. The hot solution keeps its colour for a long time, but slowly develops the odour and tint of caramel. Apparently, the increased solubility of the lead salt is due to the union of the aldehyde with the metal, which then induces the polymerisation to formose. It is suggested that a similar attachment of formaldehyde to magnesium in the chlorophyll may precede the production of formose in green plants. J. C. W.

Preparation of Aldol. N. GRÜNSTEIN (U.S. Pat., 1234156 and Brit Pat., 101636; from *J. Soc. Chem. Ind.*, 1917, 36, 1064).—Acetaldehyde, mixed with a little water, is treated with the oxide of an alkaline earth metal, such as strontium oxide. The resulting solution is neutralised with acid and distilled in a vacuum. Alkaline-earth carbides may be added to serve as catalysts, and the reaction may be started with only part of the acetaldehyde, the remainder being added as the reaction proceeds. H. W.

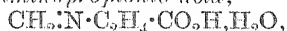
Reduction of Aliphatic Nitrites to Amines. PANCHANAN NEOGI and TARINI CHARAN CHOWDHURI (*F.*, 1917, 111, 899—902).—Gaudion (*A.*, 1912, i, 163) has described the reduction of aliphatic nitrites to mixtures of primary, secondary, and tertiary amines by hydrogen in the presence of finely divided nickel at 220 — 230° . If nickelised asbestos is used, the reduction proceeds readily at 125 — 130° , and the primary amine alone is produced. This temperature is favourable to the conversion of the nitrite into the nitro-paraffin (compare *A.*, 1916, i, 626). J. C. W.

Transformation of Secondary and Tertiary Aliphatic Amines into Nitriles. ALPH. MAILHE and F. DE GODON (*Compt. rend.*, 1917, 165, 557—559).—When the vapour of diisoamylamine is passed over nickel at 320 — 330° it is decomposed, the products

being hydrogen, an unsaturated hydrocarbon, some *triisoomylamine*, and some *isovaleronitrile*. When the vapour of *triisoomylamine* is passed over nickel at 360—370° it yields hydrogen, an unsaturated hydrocarbon, and some *isovaleronitrile*.
W. G.

Methyleneamino-acids. HARTWIG FRANZEN and ERNST FELLNER (*J. pr. Chem.*, 1917, [ii], 95, 299—311).—In only a few cases can methyleneamino-acids be prepared by evaporating solutions of the acids with formaldehyde, or by adding alcohol to concentrated solutions of the acids mixed with formaldehyde. The salts, however, are comparatively stable in cold water, and can be obtained by evaporation. They are mostly freely soluble, but some can be prepared as precipitates by double decomposition between a very soluble salt and a suitable compound of the other metal. The action of boiling water on the compounds is being investigated.

Methyleneaminoacetic acid yields a *barium* salt, $4\text{H}_2\text{O}$, a *calcium* salt, $4\text{H}_2\text{O}$, and a bluish-violet *copper* salt, $2\text{H}_2\text{O}$. *Methyleneglycylglycine*, $\text{CH}_2\text{N}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $2\text{H}_2\text{O}$, a hygroscopic powder, forms a *barium* salt, $4\text{H}_2\text{O}$. α -Methyleneaminopropionic acid gives a *barium* salt, $4\text{H}_2\text{O}$, a *calcium* salt, $2\text{H}_2\text{O}$, and a *copper* salt, $2\text{H}_2\text{O}$. β -Methylenecaminopropionic acid,



yields *calcium* and *barium* salts, both with $2\text{H}_2\text{O}$. *Methylenephénylalanine* and its *copper* salt crystallise with $2\text{H}_2\text{O}$, the *barium* salt with $1\text{H}_2\text{O}$. Methyleneasparagine gives a *barium* salt, $3\text{H}_2\text{O}$, and a *calcium* salt, $4\text{H}_2\text{O}$.
J. C. W.

Desulphurisation of Thiocarbamides (Formation of Carbamide). ERNST SCHMIDT (*Arch. Pharm.*, 1917, 255, 338—351).—Whilst ψ -thiohydantoin yields guanidine and oxalic acid when heated with mercuric oxide in concentrated aqueous ammonia, lead ψ -thiohydantoin heated with aqueous ammonia in a sealed tube at 115—120° yields, in addition to lead sulphide, acetic acid, and other substances, carbamide in considerable quantity. This formation of carbamide is all the more astonishing because Hofmann in his classical researches on the desulphurisation of thiocarbamides states that not a trace of carbamide is formed when thiocarbamide is desulphurised.

Employing xanthidrol, which Fosse has shown will detect carbamide in a dilution of one part in a million, as the reagent, the author now shows that carbamide is produced, although only in very small quantity, when thiocarbamide in aqueous solution containing a little ammonium thiocyanate is desulphurised by mercuric oxide. Whether the carbamide is formed directly from the thiocarbamide by the replacement of the sulphur atom by an oxygen atom or by a secondary reaction from the cyanamide, which is also produced by the desulphurisation, cannot be stated, because a solution of cyanamide under the same conditions also gives a precipitate of xanthidrol-carbamide.

Dicyanodiamide, guanidine, creatine, and creatinine do not yield

precipitates with xanthydrol, but thiocarbamide, hydantoin, and thiohydantoin do.

Carbamide is also formed, probably at the expense of the cyanamide, when thiocarbamide is desulphurised by silver nitrate or lead acetate in aqueous ammonia.

C. S.

Formation of Carbamide from Cyanamide. ERNST SCHMIDT (*Arch. Pharm.*, 1917, 255, 351—357. Compare preceding abstract).—A solution of cyanamide in moist ether, after being kept for fourteen days at the ordinary temperature, deposits crystals consisting of a mixture of carbamide and dicyanodiamide; the former is best isolated by treating a glacial acetic acid solution of the mixture with a freshly prepared 3—5% solution of xanthydrol in glacial acetic acid; the quantity of the crystalline xanthydrol-carbamide compound obtained is very small, 10 grams of cyanamide yielding only 0.35 gram.

When cyanamide is repeatedly evaporated to dryness with water, carbamide is formed in slightly greater quantity, 10 grams of cyanamide yielding 0.68 gram of the xanthydrol compound. A yet larger amount of carbamide is formed when cyanamide is repeatedly evaporated to dryness with a solution of hydrogen peroxide. When a solution of cyanamide in moist ether is treated with an ethereal solution of oxalic acid, a precipitate of carbamide oxalate is rapidly obtained.

C. S.

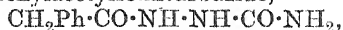
The Prussian Blue Hydrosol. WILHELM BACHMANN (*Zeitsch. anorg. Chem.*, 1917, 100, 77—94).—The green solutions obtained by adding a large excess of potassium ferrocyanide to ferric chloride do not contain a definite green double salt or other compound. The addition of salts, alcohol, or hydrochloric acid precipitates the ordinary blue solid, and the same product is obtained even by the addition of a concentrated solution of potassium ferrocyanide. The same green shade may be obtained by adding a dilute solution of colloidal ferric hydroxide to a blue solution of ferric ferrocyanide.

Ultramicroscopical examination shows that the fineness of the particles of the hydrosol increases with increasing proportion of potassium ferrocyanide, and the change to blue on addition of salts is accompanied by increasing coarseness of particles. Either the residue obtained by ultra-filtration or a fresh precipitate of 'insoluble' Prussian blue may be brought into the state of a hydrosol by addition of potassium ferrocyanide. The particles are negatively charged in a solution containing an excess of potassium ferrocyanide, but positively charged in presence of an excess of ferric chloride. Analysis of the precipitate from a green solution shows the presence of ferric hydroxide. The colour is therefore a mixed colour, resulting from the blue of Prussian blue and the yellow of colloidal ferric hydroxide.

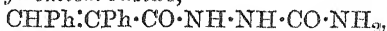
C. H. D.

Semicarbazones of α -Ketonic Acids. Acylsemicarbazides and Acylsemicarbazic Acids. J. BOUGAULT (*Bull. Soc. chim.*, 1917, [iv], 21, 180—190).—A more detailed account of work already

published (compare this vol., i, 417). The following semicarbazides are described. Phenylacetylsemicarbazide,



m. p. 156°, giving a *hydrochloride*, m. p. 170°; *α*-dimethylpropionoylsemicarbazide, $\text{CMe}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, m. p. 215°; *α*-phenylcinnamoylsemicarbazide,



m. p. 230°, giving a *hydrochloride*, m. p. 210°. All these semicarbazides are hydrolysed by dilute acids or alkalis, giving the free acid, hydrazine, carbon dioxide, and ammonia. They are oxidised by alkaline hypiodites or hypobromites, giving the salt of the acid, the alkali cyanate, and nitrogen.

W. G.

Coal Distillation under Pressure. J. H. CAPPS and G. A. HULETT (*J. Ind. Eng. Chem.*, 1917, **9**, 927—935).—In the distillation of coal, increase of pressure up to 20 atmospheres causes a decrease in the amounts of high boiling compounds and an increase in the amounts of low boiling compounds present in the vapours evolved below 600°; the quantity of low boiling aromatic substances in these oils is also increased. These results are due to “cracking” or thermal decomposition of the vapours of the heavy compounds. Increased pressure also, in many cases, reduces the quantities of phenols and acid substances in the distilled oils. Further, a larger amount of coke is obtained; the calorific value of the coke is increased, whilst the amounts of nitrogen, oxygen, sulphur, and volatile substances contained in it are decreased. The volume of gas evolved from coal below 600° is increased when the coal is distilled under pressure.

W. P. S.

Preparation of Phenol [from Cresols]. H. TERRISSE (Brit. Pat., 108938; from *J. Soc. Chem. Ind.*, 1917, **36**, 1091).—A mixture of cresols is fused with a large excess of sodium or potassium hydroxide and treated with an oxidising agent, such as copper oxide or peroxide of lead, manganese, barium, iron, or the like, in order to convert the cresols into the corresponding hydroxybenzoic acids. The product may be treated in one of two methods: (1) The fused mass is cooled on iron plates, pulverised, and heated at about 300° in iron tubes through which a current of carbon dioxide is passed. The phenol is condensed in suitable receivers. (2) The free hydroxybenzoic acids are isolated, dried, and heated in a still with crude anthracene oil at about 250°, when carbon dioxide is liberated and phenol distils over. The second method is not so satisfactory as the first, owing to the large amount of acid required to neutralise the alkali hydroxide; also, in the first method, the residual alkali carbonate can be causticised and used again.

H. W.

Solubility of Thymol in Mixtures of Water and Glycerol. M. MARQUINA (*Anal. Fis. Quim.*, 1917, **15**, 262—271).—At 25°, 100 parts of water dissolve 0.0952 part of thymol, and 100 parts of glycerol 1.71 parts of thymol. For mixtures of the two solvents, the solubility of thymol increases with the percentage of glycerol.

A. J. W.

Polymerides of Methylchavicol. P. VAN ROMBURGH and J. M. VAN DER ZANDEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 64—65).—A further study of the polymerides of methylchavicol obtained by heating it in a sealed tube at 250° for forty-eight hours (compare A., 1909, i, 597). The compound, m. p. 166°, gives a *bromide*, m. p. 139°. The compound, m. p. 98°, when oxidised with potassium permanganate in acetone solution, gives, in addition to anisic acid, an *acid*, $C_{12}H_{16}O_3$, m. p. 113°, which on further oxidation gives a second *acid*, m. p. 138°. Oxidation of the compound, m. p. 166°, only yields anisic acid. *p*-Tolyl methyl ether has been isolated from the products produced by heating methylchavicol as described above. W. G.

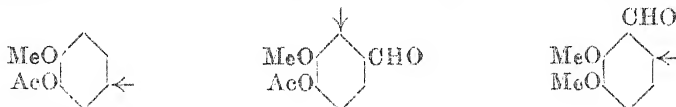
Synthesis of 4-Hydroxy-1- β -aminoethylnaphthalene [4- β -Aminoethyl- α -naphthol]. A. WINDAUS and DAISY BERNTHUSEN-BUCHNER (*Ber.*, 1917, **50**, 1120—1123).—This base has been synthesised in order to compare its physiological activity with that of adrenaline and simple phenolic bases generally; unlike *p*-hydroxyphenylethylamine, the simplest prototype of adrenaline, it is only very slightly active.

4-Methoxy- α -naphthaldehyde is converted into the corresponding acrylic acid by Perkin's method (Rousset, A., 1899, i, 296), and this is reduced by means of hydrogen and colloidal palladium to β -4-methoxy-1-naphthylpropionic acid, which crystallises in glistening needles, m. p. 165—166°. The ethyl ester is converted into the *hydrazide*, bundles of needles, m. p. 155—156°, then into the azide, a yellow powder, and this is transformed into the urethane by boiling with alcohol, as usual. *Ethyl β -4-methoxy-1-naphthylethylcarbamate*, $OMe \cdot C_{10}H_7 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CO_2Et$, crystallises in white needles, m. p. 116—117°, and is hydrolysed by prolonged boiling with hydrochloric acid to the *hydrochloride* of β -4-hydroxy-1-naphthylethylamine (4- β -aminoethyl- α -naphthol), $C_{12}H_{13}ON \cdot HCl$, glistening, quadratic leaflets, m. p. 239—240° (decomp.). The base forms a *dibenzoyl* derivative, m. p. 203—204°, and a *diacetyl* compound, m. p. 139—140°. J. C. W.

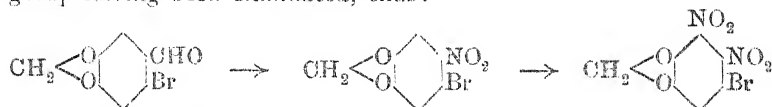
Experiments on the Orientation of Substituted Catechol Ethers. THOMAS GILBERT HENRY JONES and ROBERT ROBINSON (*T.*, 1917, **111**, 903—929).—A number of observations on the orientation of members of the series of catechol ethers are recorded. Extensive references to earlier work by Robinson and others are supplemented by a number of new facts.

I. *Substitution in Catechol Dimethyl and Methylene Ethers, and their Derivatives.*—(a) Only mono-derivatives, substituted in position 4, are obtained by direct attack on the catechol ethers. (b) With only two authenticated exceptions, di-substitution gives rise to the 4:5-derivatives. (c) In the preparation of 3:4:5-derivatives from a 4:5-substituted catechol ether, the new substituent enters the ortho-position with regard to the more negative of the groups occupying positions 4 and 5, unless the more positive group is powerfully ortho-directive.

II. *Influence of a Negative Group on a Positive Group in the Meta-position.*—Substitution in a compound which contains a negative group in the meta-position with regard to a positive group takes place at the position between these two groups, unless it is already occupied by another positive group, when the new substituent enters the para-position; for example, whilst acetylguaiacol is nitrated in the para-position with respect to the methoxy-group, acetylvanillin is attacked between the methoxy- and aldehydo-groups, and veratraldehyde next to the aldehydo-group, thus:

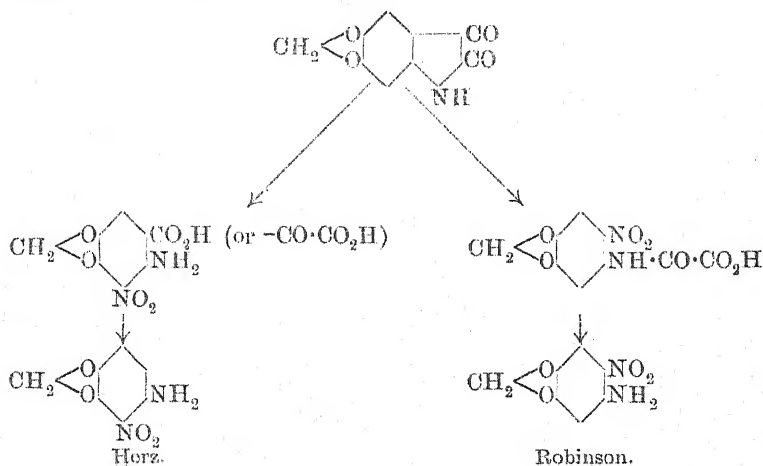


III. *Nitration of Bromopiperonaldehyde.*—Oelker (A., 1891, 1474) described a "bromonitropiperonaldehyde," m. p. 89° , and a "bromodinitropiperonaldehyde," m. p. 172° , as the products of the nitration of 6-bromopiperonaldehyde. These compounds are now shown to be nitrated bromocatechol methylene ethers, the aldehydo-group having been eliminated, thus:



The dinitro-compound loses bromine on reduction to the diamine, but the corresponding veratrole derivative retains its bromine and yields a bromodiaminoveratrole.

IV. *Action of Nitric Acid on Methyleneedioxyisatin.*—When methylenedioxyisatin is oxidised by nitric acid, an acid is produced which loses carbon dioxide on treatment with sodium carbonate, yielding a nitroamine (Herz, A., 1905, i, 778). A correct interpretation of this reaction is now given, thus:



V. *A Reaction of Piperonylic Acid.*—When piperonylic acid in sodium carbonate solution, but not in acetic acid, is treated with bromine water, but not with sodium hypobromite, 4:5-dibromocatechol methylene ether is precipitated. This forms a pale yellow solution in sulphuric acid, which is changed to crimson on the addition of a trace of nitric acid.

In the above reaction, the carboxyl group is displaced by bromine and then the monobromo-derivative is further brominated. Similarly, 4:5-dimethoxy-*o*-toluic acid yields 6-bromohomoveratrole. Apparently, the reaction is fairly general and may help in the identification of acids derived from alkaloids and other natural products, as Perkin has already shown (T., 1916, 109, 918).

VI. *Phenanthraphenazine Derivatives.*—Many *o*-dinitro- and *o*-nitroamino-compounds have been characterised by reducing them to *o*-diamines and, without isolation, converting these by means of phenanthraquinone into phenanthraphenazines. The ethers of 1:2-dihydroxyphenanthraphenazine are bright yellow and exhibit green fluorescence in neutral solvents, whilst ethers of 2:3-dihydroxyphenanthraphenazine are pale yellow and give almost colourless solutions with intense violet fluorescence. This can be turned to practical account in deciding whether a plant product is a veratrole derivative substituted only in positions 4 or 4 and 5, positive results being obtained in many cases with as little as 0.05 gram of material.



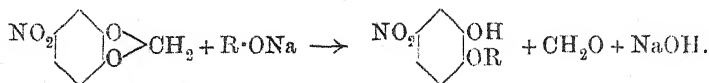
VII. *A New Heterocyclic Nucleus.*—An unusual result is recorded in the reduction of 4:5-dinitroveratrole. An orange-yellow product is obtained of the formula $C_{16}H_{16}O_6N_4S$, which is

best represented by the annexed formula. The SN_3 -grouping is designated "thiotriazo."

For experimental details, see original.

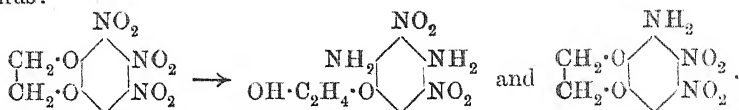
J. C. W.

The Scission of certain Substituted Cyclic Catechol Ethers. GERTRUDE MAUD ROBINSON and ROBERT ROBINSON (T., 1917, 111, 929–940).—When 4-nitrocatechol methylene ether is warmed with sodium methoxide or ethoxide solution, a 5-nitro-2-alkyloxyphenol is obtained, according to the scheme:



The corresponding ethylene ether, however, does not react in this way, but a scission of the ethylenedioxy-ring has been examined in the case of 4:5:6-trinitroethylenedioxybenzene. This reacts with ammonia to form two compounds, in one of which the ring has been opened by the addition of the elements of ammonia and the 5-nitro-group replaced by the amino-group, whilst in the other the nitro-

group in position 6 has been displaced by the amino-group, thus:



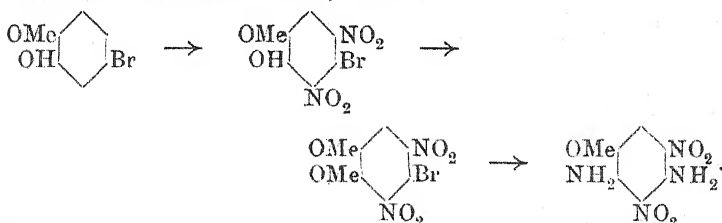
The constitution of the former compound is proved by its conversion, through simple stages, into the known 3:5-dinitro-2:4-diaminoanisole, and that of the latter by the production from it of 4:5-dinitroethylenedioxybenzene. The weak attachment of the 6-nitro-group in the trinitroethylenedioxybenzene is probably due to the proximity of the side ring, just as the α -position in naphthalene is the most open to attack.

Cardwell and Robinson (A., 1915, i, 134) showed that 5-nitroveratrole yields 5-nitroguaiacol on hydrolysis with hydrobromic acid. Similarly, the diethoxy-compound forms 5-nitro-2-ethoxyphenol. The benzoate of this may be obtained, alternatively, by nitrating 2-benzoyloxyphenetole.

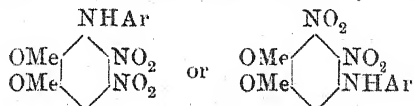
For experimental details, see original.

J. C. W.

5-Bromoguaiacol and some Derivatives. ELLEN MARGARET HINDMARSH, ISABEL KNIGHT, and ROBERT ROBINSON (T., 1917, 111, 940—946).—The methoxy-group of acyl derivatives of guaiacol has a far greater orienting influence than the acyloxy-group, and accordingly, bromination leads to the acyl derivatives of 5-bromoguaiacol. The free phenol behaves normally on further bromination, giving 4:5-dibromoguaiacol. With nitric acid, it reacts to form 5-bromo-4:6-dinitroguaiacol, but no mono-derivative has been obtained. The constitution of this is proved by the conversion of its methyl ether, by means of alcoholic ammonia, into 3:5-dinitro-2:4-diaminoanisole, thus:



The bromine atom in the dimethyl ether is comparatively firmly attached. The reaction with ammonia is very sluggish, and methylamine reacts in a similar way. Aniline and *p*-toluidine, however, give different products, represented by the formulæ



For experimental details, see the original.

J. C. W.

*d d**

1:5-Dihydroxynaphthalene. II. OTTO FISCHER [with CONSTANCE BAUER] (*J. pr. Chem.*, 1917, [ii], 95, 261—266. Compare A., 1916, i, 718).—There are in 1:5-dihydroxynaphthalene two positions, namely, 2 and 4, at which substitution takes place readily. It has already been shown that the compound only yields a mononitroso-derivative, in which position 2 is attacked, whilst most diazonium salts also only give monoazo-compounds. Position 4 is usually affected in the latter reaction, but, contrary to other diazonium salts, diazotised phenolic bases attack position 2. The constitutions of the azo-dyes may be determined by reduction to the corresponding amines.

2-Nitroso-1:5-dihydroxynaphthalene is reduced by means of phenylhydrazine to 2-amino-1:5-dihydroxynaphthalene, which crystallises in almost colourless, stellate groups, but is very unstable if exposed to air and light in a moist condition. The hydrochloride forms pale grey needles, and a sparingly soluble stannichloride is obtained if stannous chloride is the reducing agent. The amine resembles 2-amino- α -naphthol in its behaviour towards ferric chloride in acid solutions. A reddish-violet coloration is produced, which changes to deep reddish-brown on adding more ferric chloride, and finally deep red needles separate.

4-Benzeneazo-1:5-dihydroxynaphthalene (*ibid.*) is reduced by stannous chloride to 4-amino-1:5-dihydroxynaphthalene hydrochloride, which gives dark yellow shades, and finally yellow needles, with ferric chloride.

Diazotised *o*-aminophenol couples with 1:5-dihydroxynaphthalene to give 2-*o*-hydroxybenzeneazo-1:5-dihydroxynaphthalene, which is a very dark red powder with green reflex. This, and diamond-black-P.V. (1:5-dihydroxynaphthalene-4-azo-2'-phenol-5'-sulphonic acid), give 2-amino-1:5-dihydroxynaphthalene on reduction. Diazotised *o*- and *m*-aminobenzoic acids yield 4-*o*-carboxybenzeneazo-1:5-dihydroxynaphthalene [dark green, lustrous needles, m. p. 257° (decomp.)] and the 4-*m*-carboxybenzeneazo-compound (a very dark red powder with green reflex) respectively. J. C. W.

Condensation, under the action of Potassium Hydroxide, of cycloHexanol with sec-Butyl Alcohol; Synthesis of α -cyclo-Hexylbutan- β -ol. MARCEL GUERBET (*Compt. rend.*, 1917, 165, 559—561. Compare this vol., i, 453).—When cyclohexanol is heated with sec-butyl alcohol and anhydrous potassium hydroxide in a sealed tube at 210—220° for twenty-four hours, it yields α -cyclohexylbutan- β -ol, b. p. 126—127°/31 mm., D_4^{20} 0.9463, giving an acetate, b. p. 129—130°/31 mm., and a phenylcarbamate, m. p. 76°. The alcohol when oxidised with chromic acid yields cyclohexylmethyl ethyl ketone, $C_6H_{11}\cdot CH_2\cdot COEt$, b. p. 123—124°/31 mm., D_4^{20} 0.917, giving a semicarbazone, m. p. 145—146°.

W. G.

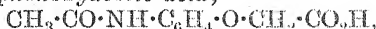
Preparation of Acylhydroxylamides from the [Oximes] of α -Ketonic Acids. J. BOUGAULT (*Compt. rend.*, 1917, 165, 592—594).—With iodine in the presence of sodium carbonate or

hydrogen carbonate, the oximes of α -ketonic acids undergo oxidation, giving acylhydroxylamides, thus: $\text{CH}_2\text{Ph}\cdot\text{C}(\text{CO}_2\text{H})\text{:NOH} + \text{O}=\text{CO}_2 + \text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$, a secondary reaction also occurring, the oxime being dehydrated, giving a nitrile. In this way, three such acylhydroxylamides have been prepared, namely, *benzoylhydroxylamide*, $\text{COPh}\cdot\text{NH}\cdot\text{OH}$, m. p. 108° ; *phenylacetylhydroxylamide*, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$, m. p. 75° ; and *phenylpropionylhydroxylamide*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$, a liquid. These acylhydroxylamides differ from the isomeric hydroxamic acids in that they are not readily hydrolysed, and with alkali do not give substituted carbamides, but are decomposed, giving a mixture of acids.

W. G.

Nitro- and Amino-phenoxyacetic Acids. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1917, **39**, 2188—2224).—An account of the preparation of a large number of these acids and their derivatives. The nitrophenoxyacetic acids may be prepared by Kym's method (compare A., 1897, i, 283) and then reduced to the corresponding amino-acids. A more satisfactory way, particularly for the *p*-amino-acids, is to use Howard's method (compare A., 1897, i, 283), and boil the acetylaminophenol and chloroacetic acid with aqueous sodium hydroxide. The following compounds are described.

o-Acetylaminophenoxyacetic acid,



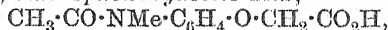
m. p. $153\text{--}154^\circ$ (corr.), which when boiled with hydrochloric acid gave *o*-aminophenoxyacetic anhydride, m. p. $173\text{--}173.5^\circ$ (corr.) (Thate gives $166\text{--}167^\circ$; compare A., 1884, 1170); *m*-aminophenoxyacetic acid, m. p. $207\text{--}208^\circ$ (decomp.), giving a hydrochloride and an ethyl ester hydrochloride, m. p. $135\text{--}136.5^\circ$.

5-Nitro-2-methylphenoxyacetic acid, m. p. $177\text{--}177.5^\circ$ (corr.), giving *5*-amino-2-methylphenoxyacetic acid, m. p. 232° (decomp.). *3*-Nitro-4-methylphenoxyacetic acid, m. p. $151\text{--}154^\circ$ (corr.), yielding *3*-amino-4-methylphenoxyacetic acid, m. p. $235\text{--}240^\circ$ (decomp.), giving a hydrochloride.

The sodium salt of 5-nitroguaiacol when heated with ethyl chloroacetate at 150° for one and a-half hours yielded *ethyl 3-nitro-6-methoxyphenoxyacetate*, m. p. $84.5\text{--}85^\circ$ (corr.), which when warmed in aqueous-alcoholic solution with an excess of sodium hydroxide gave the free acid, m. p. $184.5\text{--}186^\circ$ (corr.), and this on reduction gave *3-amino-6-methoxyphenoxyacetic acid*, m. p. $222\text{--}224^\circ$ (decomp.), which was also obtained from 5-acetylaminoguaiacol by Howard's method, the intermediate *3-acetylamino-6-methoxyphenoxyacetic acid*, m. p. $208\text{--}210^\circ$ (corr.), being hydrolysed with hydrochloric acid.

p-Aminophenoxyacetic acid gives a *methyl ester hydrochloride*, m. p. $223\text{--}225^\circ$, and a *methyl ester*, m. p. $65\text{--}66^\circ$ (corr.).

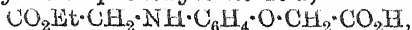
p-Acetylmethylaminophenoxyacetic acid,



m. p. $151\text{--}152^\circ$ (corr.), on hydrolysis yields *p*-methylaminophen-

oxyacetic acid, m. p. 213—214° (decomp.), giving a nitroso-compound.

p-Glycine ethyl ester phenoxyacetic acid,



m. p. 173—176° (decomp.), was prepared by boiling *p*-aminophenoxyacetic acid with ethyl chloroacetate and sodium hydroxide in aqueous-alcoholic solution, and on hydrolysis yielded *p*-glycinephenoxyacetic acid, m. p. 177—180° (decomp.), giving a hydrochloride and a dimethyl ester, m. p. 63·5—64° (corr.).

4-Acetylamino-2-methylphenoxyacetic acid, m. p. 202—204·5°, on hydrolysis yielded 4-amino-2-methylphenoxyacetic acid, which was also obtained by the reduction of 4-nitro-2-methylphenoxyacetic acid, m. p. 127·5—130·5°, with tin and hydrochloric acid. The amino-acid gives a hydrochloride, a methyl ester, 59·5—60° (corr.), giving a hydrochloride, m. p. 195—200° (decomp.), and an ethyl ester, m. p. 43—44·5° (corr.), giving a hydrochloride, m. p. 185—193° (decomp.).

4-Acetylamino-3-methylphenoxyacetic acid, m. p. 165—167·5°, yielded on hydrolysis 4-amino-3-methylphenoxyacetic acid, m. p. 217—219° (decomp.), which gave a methyl ester, m. p. 105—105·5° (corr.), giving a hydrochloride, m. p. 195—200°, and an ethyl ester, m. p. 55—55·5° (corr.), giving a hydrochloride, m. p. 203—204° (decomp.). The amino-acid, which may also be obtained by the reduction of 4-nitro-3-methylphenoxyacetic acid, m. p. 141—143°, when shaken with chloroacetyl chloride in the presence of sodium acetate, gave 4-chloroacetylamino-3-methylphenoxyacetic acid, m. p. 159—160·5° (corr.).

p-Nitroso-*o*-allylphenol, m. p. 99·5—100° (decomp.), obtained by the addition of acetic acid to a solution of *o*-allylphenol in aqueous sodium hydroxide in the presence of sodium nitrite, on reduction with ammonium sulphide gave 4-amino-2-allylphenol, m. p. 112·5—113·5° (corr.), giving an acetyl derivative, m. p. 93—93·5° (corr.), which by the usual method yielded 4-acetylamino-2-allylphenoxyacetic acid, m. p. 181—183° (corr.), which on hydrolysis gave 4-amino-2-allylphenoxyacetic acid, m. p. 193·5—194° (decomp.). A similar series of reactions, starting with *p*-nitroso-*p*-xylenol, gave 4-acetylamino-2:5-dimethylphenol, m. p. 180—181·5° (corr.), 4-acetylamino-2:5-dimethylphenoxyacetic acid, m. p. 195—197° (corr.), and 4-amino-2:5-dimethylphenoxyacetic acid, m. p. 210—215°, giving a hydrochloride, a methyl ester, m. p. 66·5—67° (corr.), and its hydrochloride, m. p. 232—234° (decomp.), and an ethyl ester, m. p. 66—66·5°, and its hydrochloride, m. p. 205—215° (decomp.).

Acetylamino-carvacrol by the usual method yielded 4-acetylamino-2-methyl-5-isopropylphenoxyacetic acid, m. p. 190—191·5° (corr.), from which 4-amino-2-methyl-5-isopropylphenoxyacetic acid, m. p. 225—226°, was prepared, giving a methyl ester, 29—30° (corr.), and its hydrochloride, m. p. 185—186° (corr.). In a similar manner, *p*-acetylaminothymol gave 4-acetylamino-3-methyl-6-isopropylphenoxyacetic acid, m. p. 186·5—188° (corr.), and 4-amino-3-methyl-6-isopropylphenoxyacetic acid, m. p. 204—206° (decomp.),

giving a *methyl ester*, an oil, and its *hydrochloride*, m. p. 169—171°.

2-Bromo-4-acetylaminophenol gave, by the usual method, 2-bromo-4-acetylaminophenoxyacetic acid, m. p. 216—219·5°, and 2-bromo-4-aminophenoxyacetic acid, m. p. 230—235°, giving a *hydrochloride* and a *methyl ester*, m. p. 74·5° (corr.), and its *hydrochloride*, m. p. 220—222°.

When *p*-acetyl-amino-*o*-cresol, in supersaturated acetic acid solution, was brominated by bromine in acetic acid at 35—40°, it yielded 6-bromo-4-acetyl-amino-*o*-cresol hydrobromide, m. p. 194—196° (decomp.), which with sodium acetate in aqueous solution gave the free acetylaminobromocresol (compare Janney, A., 1913, i, 854). The hydrobromide yielded 6-bromo-4-acetyl-amino-2-methylphenoxyacetic acid, m. p. 216—216·5° (corr.), and 6-bromo-4-amino-2-methylphenoxyacetic acid, m. p. 223° (decomp.), giving a *methyl ester*, m. p. 59° (corr.), and its *hydrochloride*, m. p. 245—250° (decomp.).

4-Acetylaminoguaiacol gave 4-acetyl-amino-6-methoxyphenoxyacetic acid, m. p. 190—191°, and 4-amino-6-methoxyphenoxyacetic acid, m. p. 190° (decomp.), giving an *ethyl ester* and its *hydrochloride*, m. p. 180—186°.

o-Aldehydophenoxyacetic acid, when added gradually to nitric acid (D 1·52) at 5°, yielded 4-nitro-6-aldehydophenoxyacetic acid, m. p. 190—192° (corr.), which gave a *phenylhydrazone*, decomp. 222°, and on oxidation with potassium permanganate in the presence of sodium carbonate, 4-nitro-6-carboxyphenoxyacetic acid, m. p. 238—240° (decomp.), which when boiled with alcohol and sulphuric acid yielded *ethyl 4-nitro-6-carbethoxyphenoxyacetate*, m. p. 75—76° (corr.). The free nitro-acid or its ester, when reduced with tin and hydrochloric acid in alcoholic solution, yielded 4-amino-6-carboxyphenoxyacetic acid, giving an *ethyl ester*, m. p. 74—76° (corr.), and its *hydrochloride*, m. p. 156—157°.

2-Hydroxy-5-acetylaminacetophenone, when boiled with chloroacetic acid and aqueous sodium hydroxide, gave 4-acetyl-amino-6-acetylphenoxyacetic acid, m. p. 223—226° (decomp.), which on hydrolysis yielded 4-amino-6-acetylphenoxyacetic acid, m. p. 145° (decomp.), giving a *methyl ester*, m. p. 141—142·5° (corr.), and its *hydrochloride*, m. p. 204—207° (decomp.).

o-Phenylenedioxyacetic acid, on nitration with nitric acid (D 1·4) at 25°, gave 4(?)-nitro-*o*-phenylenedioxyacetic acid, m. p. 181—183° (corr.), which was reduced by tin and hydrochloric acid, giving amino-*o*-phenylenedioxyacetic acid, m. p. 243—245° (decomp.).

A number of compounds similar to the aminophenoxyacetic acids and containing condensed nuclei were also prepared. 4-Acetyl-amino-1-naphthoxyacetic acid, m. p. 233—234°, giving 4-amino-1-naphthoxyacetic acid, m. p. 220—224° (decomp.). 8-Acetyl-amino-5-hydroxyquinoline, m. p. 221—223°, gives 8-acetyl-amino-5-quinolyl-oxyacetic acid, m. p. 255° (decomp.), giving 8-amino-5-quinolyl-oxyacetic acid, m. p. 225° (decomp.).

5-Amino-8-hydroxyquinoline dihydrochloride, m. p. 245° (decomp.), obtained by the reduction of the corresponding nitroso-

compound, gave 5-acetyl-amino-8-hydroxyquinoline; m. p. 221—222°, which yielded 5-acetyl-amino-8-quinolyloxyacetic acid, m. p. 253—255° (decomp.), giving a nitrate, m. p. 225—230° (decomp.), and on hydrolysis 5-amino-8-quinolyloxyacetic acid dihydrochloride, m. p. 160—162° (decomp.), giving a methyl ester, 176—177° (corr.).

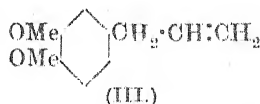
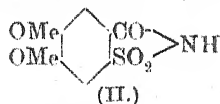
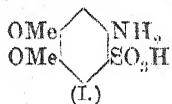
Two aminophenoxybutyric acids were also prepared, as follows. *o*-Acetylaminophenol, when boiled for three hours in alcoholic solution with sodium hydroxide and trimethylene bromide, yielded a small amount of propylenebis(*o*-acetylaminophenyl) ether,

$\text{COMe}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{COMe}$, m. p. 193·5—194·5° (corr.), and as principal product *o*-acetylaminophenoxypropyl bromide [*o*-acetylaminophenyl γ -bromopropyl ether], $\text{COMe}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, m. p. 62—62·5° (corr.), which in boiling alcoholic solution with potassium cyanide gave *o*-acetylaminophenoxybutyronitrile, m. p. 89—90° (corr.), and this when boiled with hydrochloric acid yielded *o*-amino- γ -phenoxybutyric acid hydrochloride, m. p. 180—182°. The free amino-acid, m. p. 54—57°, gives a methyl ester, m. p. 45—45·5°. A similar series of compounds was prepared starting with *p*-acetylaminophenol. *p*-Acetylaminophenoxypropyl bromide, m. p. 133—135°; *p*-acetylaminophenoxybutyronitrile, m. p. 98—100°; *p*-amino- γ -phenoxybutyric acid hydrochloride, m. p. 191—194°, and its free amino-acid, m. p. 145·5—146° (corr.).

Practically all the aminophenoxyacetic acids and their esters give colours with ferric chloride, and those containing primary amino-groups are readily diazotised, and then couple with R-salt to give soluble dyes of varying shades of red.

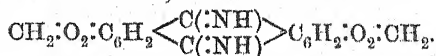
W. G.

Veratricsulphinide. JANET FORREST MCGILLIVRAY BROWN, and ROBERT ROBINSON (T., 1917, 111, 952—958).—Veratrole and homo-veratrole react smoothly with chlorosulphonic acid. Through the sulphonyl chloride, the former has been converted into 5-amino-veratrole-4-sulphonic acid (I), and the latter into veratric-6-sulphinide, or "dimethoxysaccharin," (II):



Eugenyl methyl ether (III) occurs in large quantities in the Huon Pine of Tasmania, and it was thought that an outlet might be found for it by converting it into the above "saccharin" derivative. It does not react with chlorosulphonic acid in the normal way, however, and, moreover, the veratricsulphinide is not sweet.

Other veratrole derivatives behave abnormally with chlorosulphonic acid. For example, piperonylonitrile yields the di-imide of an anthraquinone derivative, of the formula:



For experimental details, see the original.

J. C. W.

Salts and Esters of *d*-Camphoric Acid. H. THOMS and P. RUNZE (*Ber.*, 1917, 50, 1217—1221).—Camphoric acid exhibits a great tendency to form normal salts, so that, if treated with one equivalent proportion of sodium carbonate, it does not yield the sodium hydrogen salt, but a mixture of the disodium salt and free acid. Attempts have been made, however, to prepare soluble ester-salts, using phenols as one component, in view of their probable value in therapeutics.

Many aryl hydrogen camphorates were prepared by Schryver (*T.*, 1899, 75, 661). To these are now added the cresol derivatives, the *tolyl hydrogen d-camphorates*, as follows: *ortho*-, glistening needles, m. p. 127°, $[\alpha]_D^{20} + 66.18^\circ$; *meta*-, m. p. 98°; *para*-, glistening crystals, m. p. 102—103°.

Attempts to convert the *o*-tolyl ester into sodium or potassium *o*-tolyl camphorate by exact neutralisation result in the formation of the di-alkali salts, free *o*-cresol, and free camphoric acid. If the solution of the ester in alcohol and ether is mixed with alcoholic ammonia, however, *ammonium o-tolyl camphorate* is precipitated. The *methylammonium* and *diethylammonium* (m. p. 109—110°) salts can be obtained in the same way. The ammonium salts are decomposed by boiling alcohol. *Cupric o-tolyl camphorate*, $(C_6H_4Me \cdot CO_2 \cdot C_8H_{11} \cdot CO_2)_2Cu$, can also be prepared by immediately adding copper sulphate to a mixture of the ester and one equivalent of sodium hydroxide. It is decomposed by boiling water into copper camphorate, camphoric acid, and *o*-cresol.

No salts of the above type could be obtained with cyclic bases, and an attempt to prepare *o*-tolyl camphoranilate resulted in the formation of free camphoranilic acid, m. p. 204°. J. C. W.

Demonstration of the Scission of Salts of Organic Acids by means of Conductivity Determinations. H. THOMS and G. K. W. ZEHRFELD (*Ber.*, 1917, 50, 1221—1227).—Küster has shown that in the case of many of the mono- and di-basic acids exact titrations can be made by determining the points of abrupt change (often minima) in the conductivity curve as alkali is added to the acid, but he pointed out that the critical change sets in too soon in the case of some weak acids (*A.*, 1903, ii, 611; 1905, ii, 55). Camphoric acid is a good example of the latter class. If sodium hydroxide is gradually added to a solution of the acid, the conductivity falls for a brief interval, but very soon proceeds to rise until the acid is neutralised. For a time, therefore, the solution contains a substance of lower conductivity than the free acid, which can only be sodium hydrogen camphorate. Küster would have explained the subsequent quick change in the conductivity by assuming that ions of this salt were rapidly appearing in place of undissociated acid molecules, but there is another interpretation. From a solution of camphoric acid with one equivalent of alkali, that is, apparently, a solution of the acid salt, ether will extract nearly half of the acid in the free state, leaving the normal salt (see following abstract). In other words, as Jungfleisch and Landrieu also demonstrated (*A.*,

1914, i, 416), sodium hydrogen camphorate is decomposed by water into the normal salt and free acid. The change in conductivity is therefore due to a new grouping of the ions already present. The change sets in later if the solutions are more concentrated, which supports the view that the effect is due to the action of water.

J. C. W.

Scission of Acid Salts into Normal Salts and Free Acids in Aqueous Solutions. H. THOMS and TH. SABALITSCHKA (*Ber.*, 1917, 50, 1227—1235).—Acid salts of dibasic acids, MHX , in aqueous solutions give the ions M' and HX' , and the latter ion may be resolved further into H' and X'' . These ions may subsequently re-unite in all possible ways, to give molecules of the normal or acid salt and free acid. The tendency will be towards the production of the least soluble or least dissociated molecules, under the given conditions. If the new product is removed, the new change will continue in the new direction.

In the case of potassium hydrogen sulphate, for example, it might be possible for potassium sulphate to crystallise out if its solubility-product is surpassed. This has actually been achieved by repeatedly precipitating the salt from a solution of the acid sulphate by means of alcohol. After four precipitations, pure potassium sulphate was obtained.

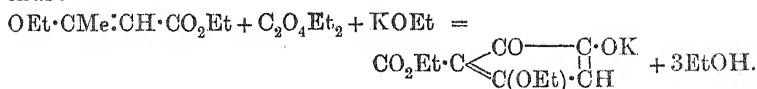
On the other hand, it is possible in the case of some organic acids to remove the free acid by extraction with ether, and so to obtain the neutral salt. In the case of the alkali hydrogen camphorates, the salts are already very largely resolved into normal salts and free acids, so that one extraction with ether will remove nearly half of the total amount of acid. The influence of the metallic ion is not very great, but ether will extract slightly more acid from a potassium hydrogen camphorate solution than from a sodium, lithium, or ammonium salt solution under the same conditions. *iso*Camphoric and *isophthalic* acid salts behave similarly. The same is true for sodium hydrogen phthalate solutions, but here the quantitative control of the experiments is weakened by two other facts. First, phthalic acid so easily changes into the anhydride that ethereal solutions lose water on evaporation, and secondly, normal sodium phthalate is hydrolysed by water and so yields up some phthalic acid to ether.

Ether does not extract oxalic acid from solutions of potassium hydrogen oxalate, but does from the quadroxalate, leaving the acid salt. Apparently, the $\text{CO}_2\text{H}\cdot\text{CO}_2^-$ ion does not dissociate to any appreciable extent, or, rather, the K' , H' , and $(\text{CO}_2)_2''$ ions do not tend to reunite to form new molecules.

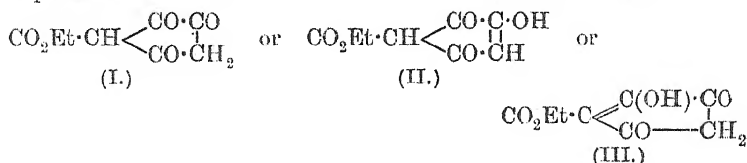
J. C. W.

Condensation of Ethyl Oxalate with Ethyl Ethoxycrotonate, Ethoxypropene, and Acetonedietiethylacetal. WILHELM WISLIGENUS and KARL SCHÖLLKOPF (*J. pr. Chem.*, 1917, [ii], 95, 269—298).—Ethyl oxalate and ethyl β -ethoxycrotonate

react in the presence of potassium ethoxide to form a deep red salt, thus:



When this is acidified, an ethyl radicle is eliminated and an ester is produced which reacts as a triketone or mono-enol, thus:



The properties and reactions of this ester, "ethyl oxalylacetoacetate," form the chief feature of this communication.

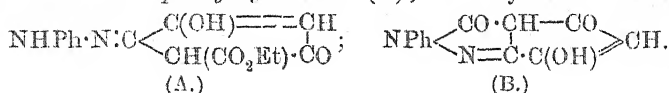
The above-mentioned salt, *potassium ethyl 4-hydroxy-2-ethoxy- $\Delta^{1:3}$ -cyclopentadiene-5-one-1-carboxylate*, crystallises in deep purplish-red bundles of microscopic needles, m. p. 240° (decomp.). It decomposes slowly in contact with cold water, better on boiling with 96% alcohol, yielding the potassium salt of *4-ethoxy- α -pyrone-6-carboxylic acid*, $\text{CO}_2\text{K} \cdot \text{C} \begin{array}{l} \text{O} \\ \text{CH} \cdot \text{C}(\text{OEt}) \end{array} \text{CH}$. The free acid crystallises in small, colourless needles, which melt with evolution of gas when plunged in a bath at 150° , then solidify again, and finally melt at 164 – 166° . The *ethyl ester*, m. p. 84 – 86° , changes into the original red potassium salt when mixed with potassium ethoxide, and reacts with ammonia to form *ethyl 2:4-dihydroxypyridine-6-carboxylate*, m. p. 198 – 200° .

The *enolic form* of "*ethyl oxalylacetoacetate*," the " α "-modification (II) or (III), is best obtained by mixing the red salt with concentrated sulphuric acid in the presence of ether, and then extracting the solid ester from the potassium hydrogen sulphate by means of ether. It crystallises in pale yellow needles, m. p. 145 – 150° (decomp.), gives the typical ferric chloride and Laubenheimer reactions, yields a yellow precipitate with potassium ethoxide, but does not form esters. The β -modification, *ethyl cyclopentane-2:4:5-trione-1-carboxylate* (I), is obtained by boiling the enol with water, cooling, and adding a large excess of sulphuric acid. It crystallises in microscopic, yellow, elongated leaflets, m. p. 105 – 110° (decomp.), gives first a yellow and then a red precipitate with potassium ethoxide, and decomposes on boiling with solvents.

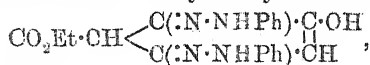
The two esters behave in a remarkable manner when attempts are made to isolate their salts. The α -form gives a normal, very pale yellow *pyridine salt*, $\text{C}_8\text{H}_8\text{O}_5 \cdot \text{C}_5\text{H}_5\text{N} \cdot 3\text{H}_2\text{O}$, m. p. 55° (anhydrous, m. p. 98°), when mixed with the base in moist ethyl acetate, and this yields the enol again when mixed with concentrated sulphuric acid and ether. When boiled with alcohol, this salt changes into an abnormal, orange-red salt, $\text{C}_{16}\text{H}_{14}\text{O}_9 \cdot \text{C}_5\text{H}_5\text{N}$, from which the β -form is recoverable. This salt may be obtained by boiling the α -form, but

better the β -modification, with pyridine and alcohol or acetone, thus: $2C_8H_8O_5 + C_6H_5N = C_{16}H_{11}O_9, C_6H_5N + H_2O$. Either ester yields a corresponding abnormal *potassium* salt, $C_{16}H_{13}O_9K$ (bundles of yellow needles), when warmed with aqueous-alcoholic potassium hydroxide, and the β -form gives the similar *ammonium* salt (golden-yellow, felted needles) with alcoholic ammonia; these give the β -ester on acidifying.

The α -ester reacts with one molecular proportion of phenylhydrazine to form a *phenylhydrazone* (A); this crystallises in small,

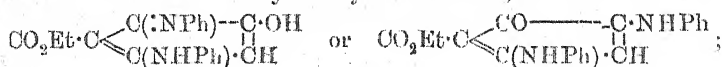


yellow tablets, m. p. 184—186° (decomp.), and changes into a *pyrazolone* derivative (B), stellate groups of yellow needles, m. p. about 190° (decomp.), on boiling with glacial acetic acid. With two molecular proportions of phenylhydrazine, the ester yields an additive compound of phenylhydrazine and the above phenylhydrazone; this crystallises in pale yellow needles, m. p. 148° (decomp.), and changes into a *diphenylhydrazone* of "ethyl oxalylacetoacetate,"

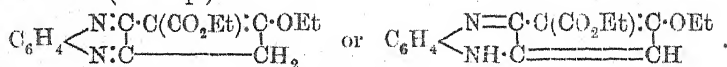


when boiled with methyl alcohol. The same compound is formed as a precipitate when a solution of the base in dilute acetic acid is added to an aqueous solution of the original red potassium salt; it crystallises in very pale brown, rhombic leaflets, m. p. 198—202° (decomp.), which change in contact with methyl alcohol into curved filaments (additive compound). The diphenylhydrazone also changes into an *isomeride*, deep, greenish-yellow tablets, m. p. 198—200°, when boiled with glacial acetic acid or xylene, but not if heated alone. The β -ester forms a sparingly soluble, dark red *phenylhydrazone*.

A solution of the original red salt gives a precipitate of a *di-anilino*-derivative of "ethyl oxalylacetoacetate,"



this crystallises in dark, ruby-red, elongated, glistening leaflets. The same salt reacts with *o*-phenylenediamine to form a *phenazine* of "ethyl oxalylethoxyerotonate," yellowish-red needles, m. p. 183—185° (decomp.):



The above α -oxalylacetoacetic ester also yields a *phenazine*, $C_{14}H_{12}O_3N_2$, which crystallises in bundles of slender, yellow needles, decomp. 210—220°, and exhibits a bright, bluish-green fluorescence in organic solvents. This phenazine differs from the foregoing one by the ethyl radicle of the ethoxyl group, and it can also be obtained by boiling the first phenazine with dilute acetic acid.

The initial red salt, or an alkaline solution of the above α -ester, also reacts with benzenediazonium chloride to form *ethyl 3-hydroxy-4-benzeneazo- Δ^3 -cyclopentene-2:5-dione-1-carboxylate* ("*ethyl benzeneazo-oxalylacetoacetate*"), $\text{CO}_2\text{Et}\cdot\text{CH} < \begin{smallmatrix} \text{CO}\cdot\text{C}\cdot\text{OH} \\ \text{CO}\cdot\text{C}\cdot\text{N}:\text{NPh} \end{smallmatrix}$, which crystallises in dark red, glistening, flat needles, decomp. about 180° .

Ethyl oxalate also combines with β -ethoxypropene (*isopropenyl ethyl ether*) and acetonedietethylacetal ($\beta\beta$ -diethoxypropane) in the presence of potassium ethoxide, but the product is the *dipotassium salt of ethyl acetonedioxalate* (compare Willstätter and Punmerer, A., 1904, i, 973). J. C. W.

Action of Halogens on Piperonaldehyde. ANNIE MARY BLEAKLY ORR, ROBERT ROBINSON, and MARGARET MARY WILLIAMS (T., 1917, 111, 946—952).—If piperonaldehyde is treated with bromine or chlorine in neutral solvents, excellent yields of the 6-halogenopiperonaldehydes are obtained, but displacement of the aldehydo-group takes place to a considerable extent if glacial acetic acid is used as the solvent, the 4:5-dihalogenocatechol methylene ethers being formed as well. The aldehydo-group is also displaced if the halogenopiperonaldehydes are nitrated. Similarly, the carboxyl groups in piperonylic and 6-chloropiperonylic acids are displaced on adding bromine or chlorine to sodium carbonate solutions of these acids.

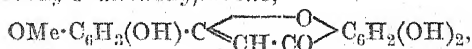
Piperonaldehyde has been converted into its corresponding alcohol and acid by the Cannizzaro reaction.

For experimental details, see the original.

J. C. W.

A New Method for Preparing Cyclic Ketones. III. and IV. ALFRED SCHAARSCHMIDT (Ber., 1917, 50, 1356—1359, 1360—1362. Compare this vol., i, 285).—Polemical. Replies to Ullmann (this vol., i, 342). J. C. W.

Homoeriodictyol. O. A. OESTERLE and R. KUENY (*Arch. Pharm.*, 1917, 255, 308—314).—Power and Tutin's homoeriodictyol (T., 1907, 91, 887), named eriodictyonone by Mossler (A., 1907, i, 947; ii, 292), has been regarded as a hydrindene derivative by the latter and as 2:4:6-trihydroxyphenyl 4-hydroxy-3-methoxystyryl ketone by Tutin (T., 1910, 97, 2054). Further evidence in support of the latter view has been obtained by the authors. Hesperetin, which is isomeric with homoeriodictyol, has already been converted into 5:7:3'-trihydroxy-4'-methoxyflavone (luteolin methyl ether, m. p. 253 — 254°) by the authors (*Arch. Pharm.*, 1915, 253, 383). So also homoeriodictyol, for which the authors find m. p. 218° (Power and Tutin give 223° ; Mossler, 214 — 215°), has been converted into a new luteolin monomethyl ether, which is 5:7:4'-trihydroxy-3'-methoxyflavone,



citron-yellow needles, m. p. 324 — 325° (decomp.), the positions of the substituents being determined by the nature of the fission pro-

ducts (phloroglucinol and ferulic acid) of homoeriodictyol. The substance is obtained as follows. Tetra-acetylhomoeeriodictyol, m. p. 154° (Power and Tutin give the same m. p.; Mossler gives 158°), is converted by bromine in chloroform into a crude bromide, a hot alcoholic solution of which is treated with 50% potassium hydroxide and subsequently with water. The new luteolin monomethyl ether is precipitated from the solution by hydrochloric acid, and is best purified through its *triacetate*, $C_{18}H_9O_6Ac_3$, faintly yellow needles, m. p. 215—216°. The triacetate yields luteolin when boiled for nine hours with equal volumes of glacial acetic acid and hydriodic acid, D 1.96.

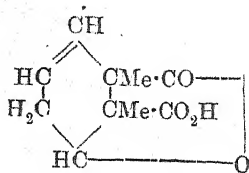
The authors direct attention to the great similarity between 5 : 7 : 4'-trihydroxy-3'-methoxyflavone and Tutin and Clewer's chrysoeriol (T., 1909, 95, 81), and hope to prove that the two substances are identical.

C. S.

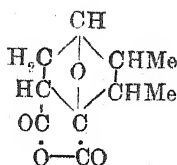
Cantharidin. VIII. Pyrogenic Decomposition of Barium Cantharate. J. GADAMER (*Arch. Pharm.*, 1917, 255, 315—337).—The only remaining point at variance with Rudolph's formula of cantharidin is the formation of α -hemellithylic acid by the pyrogenic decomposition of barium or calcium cantharate (compare Gadamer, this vol., i, 659), and this discrepancy now receives attention.

An optically not quite pure, lævorotatory *d*-cantharic acid, $[\alpha]_D -70^\circ$, is evaporated to dryness with a concentrated aqueous solution of rather more than two equivalents of barium hydroxide, and the residue is heated at about 380° for ten to twenty minutes in a current of dry hydrogen. The products are: (1) water; (2) an oil, consisting of impure cantharene; and from the residue after acidification (3) acids volatile with steam, and (4) acids non-volatile with steam. The acids under (3) are separated into (*a*) those easily soluble in water, and (*b*) those sparingly soluble in water. Two of the former are suspected from their odour to be angelic or α -methylbutyric acid and isobutyric acid, but no acids in the pure state could be isolated. The author indicates the possibility of the formation of these acids from cantharic acid (formula I).

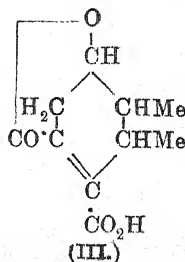
From the mixture of acids obtained under 3*b*, two acids have been isolated in a pure state, namely, α -hemellithylic and *p*-xylic (3:4-dimethylbenzoic) acids, in the proportion of 10:1. The



(I.)



(II.)



(III.)

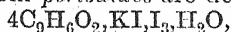
formation of these two acids would be easily explicable if cantharidin and cantharic acid contained four side chains, namely, two methyl groups in the ortho-position and also two carboxyl groups in the ortho-position to one another, as, for example, in formulæ II (cantharidin) and III (cantharic acid). The objection to any such formulæ is, however, that cantharidin must have a symmetrical structure in consequence of its formation from hydrobromocantharic acid (Gadamer, A., 1915, i, 432). There remains, therefore, no alternative but to assume that a migration of radicles (carboxyl groups) occurs during the pyrogenic decomposition of barium cantharate, and the author indicates how α -hemellithylic and p -xylic acids could be produced, by such migrations and by loss of hydrogen, from cantharic acid of the accepted formula (I).

The acids under (4) are amorphous and contain unsaturated constituents. After reduction by the Paal-Skita-Mannich method, the bulk of the mixture remains unchanged (and from it nothing of definite character has been isolated), but from the reduced portion an acid, m. p. 54.5° , has been obtained, which may be myristic acid, but is more probably α -methylmyristic acid. C. S.

Synthesis of a Crystalline β -isocurcumin. GUSTAV HELLER (*Ber.*, 1917, 50, 1244—1247. Compare A., 1915, i, 417).—A second isomeride of isocurcumin has been obtained from the product of the condensation of vanillin with acetylacetone. It occurs to the extent of 1—2% of the vanillin used, is sparingly soluble in benzene, and crystallises well only from acetic acid, with which it forms a compound, $3C_{21}H_{20}O_6 \cdot C_2H_4O_2$. This β -isocurcumin, m. p. $111-112^{\circ}$, dissolves in concentrated sulphuric acid with bright red colour and vivid blue fluorescence, and in alkali carbonates and hydroxides with much brighter red colour than that given by curcumin. It is not transformed into curcumin even at 150° , and it does not give metallic lakes, for example, with ferric chloride. Curcumin is enolic and α -isocurcumin probably a mixture (*ibid.*), β -isocurcumin is therefore to be regarded as the pure diketone, $CH_2[CO \cdot CH : CH \cdot C_6H_3(OH) \cdot OMe]_2$. J. C. W.

Periodides in the Coumarin Series. H. SIMONIS (*Ber.*, 1917, 50, 1137—1142).—Dox and Gaessler (this vol., i, 346) have recently described a compound, $(C_9H_6O_2)_4I_2$, as the product of the action of iodine and potassium iodide on coumarin. It is now shown that potassium enters into the composition of this substance, and that it is really the salt of the acid, $4C_9H_6O_2 \cdot HI \cdot I_3$, which Morgan and Micklethwait obtained by dissolving coumarin in hydriodic acid containing iodine (T., 1906, 87, 868). The potassium iodide can be replaced by other alkali iodides or bromides, or by mercuric iodide, and alkyl derivatives of coumarin, provided that the pyrone ring is intact, give similar compounds.

The following coumarin *periodides* are described:



bronze-green, scintillating needles, m. p. $87-89^{\circ}$, transformed by fuming hydrochloric acid into Morgan and Micklethwait's com-

pound; $4\text{Cou.}, \text{NaI}, \text{I}_3$, violet needles with coppery lustre, m. p. $86-87^\circ$; $4\text{Cou.}, \text{LiI}, \text{I}_3$, bronze-green, m. p. about 38° ;

$4\text{Cou.}, \text{RbI}, \text{I}_3, \text{H}_2\text{O}$, crystals with the colour of Spanish flies, m. p. $86-87^\circ$; $4\text{Cou.}, \text{CsI}, \text{I}_3, \text{H}_2\text{O}$, greenish-brown, iridescent needles, m. p. $72-73^\circ$; $4\text{Cou.}, \text{KI}, \text{HgI}_2, \text{I}_2$, bronze-brown, woolly needles, m. p. 96° ; $4\text{Cou.}, \text{KBr}, \text{I}_3$, golden-green needles, m. p. $74-76^\circ$, leaves potassium bromide on distillation.

3-Methylcoumarin gives a compound, $4\text{C}_{10}\text{H}_8\text{O}_2, \text{KI}, \text{I}_3, \text{H}_2\text{O}$, spinach-green needles, m. p. 100° , and 4:7-dimethylcoumarin yields the substance, $4\text{C}_{11}\text{H}_{10}\text{O}_2, \text{KI}, \text{I}_3$, in long, dark green needles, m. p. 115° .
J. C. W.

Researches on Pseudo-bases. II. Some Berberine Derivatives and Remarks on the Mechanism of the Condensation Reactions of Pseudo-bases. GERTRUDE MAUD ROBINSON and ROBERT ROBINSON (T., 1917, 111, 958-969. Compare T., 1914, 105, 1456).—The analogy between berberine and cotarnine has been spectrochemically demonstrated by Tinkler (T., 1911, 99, 1340) and confirmed in the case of their condensation products with acetone by Pymán (*ibid.*, 1694). Further condensation products have now been obtained, which, although much less stable than the corresponding cotarnine and hydrastinine compounds, only serve to strengthen the analogy. Compounds of the types $\psi\text{-B-CN}$, $\psi\text{-B-OMe}$, $\psi\text{-B-CH}_2\text{Bz}$, and $\psi\text{-B-CH}_2\text{NO}_2$ are described. For experimental details, see the original.

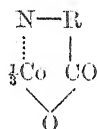
The mechanism of these pseudo-base condensations is discussed in the light of a theory which involves the conjugated partial dissociation of the reacting substances (compare Baly's "opening up the molecular force fields"), followed by direct union, and then re-distribution of the affinities within the new system. The theory is extended to a discussion of the bromination of ketones, and diazo-coupling.
J. C. W.

The Alkaloids of the Calabar Bean. VI. Constitution of Geneserine. Transformation of Eserine into Geneserine. MAX POLONOVSKI (*Bull. Soc. chim.*, 1917, [iv], 21, 191-200. Compare A., 1916, i, 284).—From a further consideration of the properties of eserine and geneserine and a study of the oxidation of eserine, the author now considers geneserine to be an eserine oxide, eserine having the constitution $\text{NMe}:\text{C}_{12}\text{H}_{11}\text{N}\cdot\text{O}\cdot\text{CO}\cdot\text{NHMe}$, and geneserine, $\text{O}:\text{NMe}:\text{C}_{12}\text{H}_{11}\text{N}\cdot\text{O}\cdot\text{CO}\cdot\text{NHMe}$. Eserine, when oxidised in alcoholic solution by hydrogen peroxide, yields geneserine, and eserethol, under similar conditions, yields geneserethol. When eserine is oxidised by potassium permanganate in the presence of dilute sulphuric acid or by dilute nitric acid, partial decomposition occurs, methylamine being liberated.
W. G.

Internally Complex Salts. XV. Isomerism and Absorption of Light of Internally Complex Salts. II. LEY and K. FICKEN (*Ber.*, 1917, 50, 1123-1137).—The optical properties of some salts of amino-acids are discussed.

I. According to Werner's theory, internally-complex salts of the type $M'''(RX)_3$ should exist as *cis*- and *trans*-isomerides, and such

are known in the case of the red and violet cobaltiglycines (A., 1909, i, 886) and cobalti- α -alanines (A., 1912, i, 243). To these are now added red and violet cobaltic picolinates. The question is considered whether stereoisomeric forms of each isomeride should not exist. It can easily be demonstrated with a model that the three



ring-systems attached to a tervalent atom, as in the annexed formula, could be so arranged in space as to provide for such stereoisomerism. However, the above red and violet salts are so indifferent that no hope of resolving them into possible optical isomerides can be entertained, but it was thought that it might perchance be possible to isolate such compounds if an optically

active amino-acid were used at the outset. Accordingly, cobaltic salts of *D*-alanine have been prepared, but only one form of each geometric isomeride has been found. The red salt forms thin needles, $[M]_{\text{red}} - 472^\circ$, in 50% sulphuric acid, and the violet salt, which is soluble in boiling 9% sulphuric acid, crystallises in rhombic tablets, $[M]_{\text{red}} + 1330^\circ$. The solutions of these salts in sulphuric acid do not change colour, but become optically inactive in the course of two years.

II. The following salts of picolinic acid have been prepared. The cupric salt crystallises in deep blue needles or bluish-violet leaflets, both with $2\text{H}_2\text{O}$. The cobaltic salt can be obtained in two forms; the violet salt, $\text{Co}(\text{C}_6\text{H}_4\text{O}_2\text{N})_3 \cdot \text{H}_2\text{O}$, crystallises in microscopic, elongated, hexagonal leaflets; the pale red salt, $2\text{H}_2\text{O}$, forms extremely slender needles which are very sparingly soluble in water, and it can be converted into the violet salt by heating with 25% acetic acid in a sealed tube at $170-180^\circ$. The chromic salt exists in red needles, with $1\text{H}_2\text{O}$, sparingly soluble in water, and in insoluble, blue crystals, $\frac{1}{2}\text{H}_2\text{O}$. The platinous salt is extremely stable, and is known only in the form of pale yellow needles.

The cobaltic salts of the amino-acids behave in a curious manner towards sodium hydroxide. Both red and violet forms are hydrolysed by the dilute alkali to cobaltic hydroxide, the violet salts also with concentrated solutions. The red forms of the cobaltic salts of glycine, alanine, and picolinic acid, however, dissolve in concentrated sodium hydroxide to give deep blue solutions resembling those of cobaltous salts.

III. The absorption spectra of red and violet cobaltic picolinates closely resemble those of the salts of glycine and alanine. The characteristic band of picolinic acid ($1/\lambda = 3800$ recip. $\text{\AA} \cdot \text{U.}$) is not exhibited; both show a band at $1/\lambda = 2700$, and another at about 1950, but the extinction in the latter case is stronger for the red form. Cobaltous picolinate, however, shows the characteristic band of the acid, but, compared with cobaltous acetate or sulphate, its chief absorption band is displaced slightly towards the short-wave end of the spectrum (1960 compared with 2080), and the extinction is much greater. The cobaltous picolinate is, therefore, also an

internally-complex salt, but of a much weaker character than the cobaltic salts. Whilst, for example, the cobaltic salts are stable towards concentrated acids, the cobaltous salt is decomposed, thus:
 $\text{CoX}_2 + 2\text{HCl} = \text{CoCl}_2 + 2\text{HX}.$

J. C. W.

Chromoisomerism of Acridinium Salts. A. HANTZSCH (*Ber.*, 1917, 50, 1204—1213. Compare A., 1916, i, 835).—A continuation of the controversy with Kehrman (compare this vol., i, 221).

Some misapprehension seems to exist as to what Hantzsch means by "chromoisomerism." He uses the term in a temporary sense only, with reference to isomerides which for the time being are only known to differ in colour, and until chemical, structural differences are revealed which would entitle them to other descriptions.

In the case of the phenylmethylacridinium sulphites, it is claimed that there is no evidence to show how they differ structurally, and so they are still called "chromo-isomerides." They have been re-investigated, and it is described how the following salts may be prepared: *yellow* series: anhydrous sulphite, hydrate ($n\text{H}_2\text{O}$?), compound with $1\text{C}_2\text{HCl}_5$; *brown* series: anhydrous salt; $\text{B}, \text{H}_2\text{O}$; B, EtOH ; $\text{B}, 2\text{EtOH}$; B, CHCl_3 ; and $\text{B}, n\text{C}_2\text{HCl}_5$?; *green* series: anhydrous salt; $\text{B}, 3\text{H}_2\text{O}$; $\text{B}, 1$ and 1.5EtOH ; B, CHCl_3 ; and $\text{B}, 1$ and $2\text{C}_2\text{HCl}_5$.

J. C. W.

Constitution of Isatin Salts. GUSTAV HELLER (*Ber.*, 1917, 50, 1199—1202. Compare this vol., i, 219).—A reply to Claasz (this vol., i, 413). Claasz stated that *N*- and *C*-metallic salts are incompatible with water, but it is shown that the *N*-sodium and *N*-potassium salts of isatin can actually be obtained as precipitates, under certain conditions, from alcoholic solutions containing small quantities of water.

J. C. W.

Theory of the Oxidation of Benzidine in its Significance for Peroxydase Investigations. W. MADELUNG (*Ber.*, 1917, 50, 1182—1187. Compare this vol., i, 285).—Polemical. A reply to Woker (this vol., i, 62, 485).

J. C. W.

Dindole. GUSTAV HELLER (*Ber.*, 1917, 50, 1202—1203. Compare Ruggli, this vol., i, 586).—Dindole is obtained in good yield by the gradual addition of zinc dust to an acetic acid solution of *oo'*-dinitrobenzil (Kliegl and Haas, A., 1911, i, 433). It is identical with Golubev's "di-iminotolane."

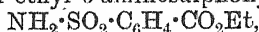
J. C. W.

Action of *p*-Nitroso-bases on Hydrazines. II. OTTO FISCHER [with M. CHUR] (*J. pr. Chem.*, 1917, [ii], 95, 266—269. Compare A., 1915, i, 907).—The product of the action of semicarbazide on *p*-nitrosodimethylaniline, namely, *p*-dimethylamino-benzenediazoxycarbamide, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{O} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, decomposes on boiling with 20% sulphuric acid according to the equation $\text{C}_9\text{H}_{13}\text{O}_2\text{N}_5 + 2\text{H}_2\text{O} = \text{N}_2 + \text{CO}_2 + 2\text{NH}_3 + \text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH} + \text{O}.$

J. C. W.

Hydrazides and Azides of Sulphocarboxylic Acids. I. Action of Hydrazine on Ethyl *o*-Aminsulphonylbenzoate.

ERNST SCHRADER (*J. pr. Chem.*, 1917, [ii], 95, 312—326).—The action of hydrazine on ethyl *o*-aminosulphonylbenzoate,



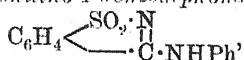
at moderate temperatures and at 125° in a sealed tube has been investigated.

When boiled with alcoholic hydrazine, the ester yields *o*-aminosulphonylbenzhydrazide, $\text{NH}_2 \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$, in very long spikes, m. p. 182°; this forms a *hydrochloride*; a *benzylidene* compound, filamentous needles, m. p. 174°; a *m*-nitrobenzylidene compound, m. p. 215°; and a *p*-methoxybenzylidene compound, pearly flakes, m. p. 184°. The same hydrazide may be obtained by boiling "saccharin" with hydrazine hydrate. When treated with nitrous acid, it is converted into *o*-aminosulphonylbenzoylazine, $\text{NH}_2 \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{N}_3$, which crystallises in snow-white needles, continually evolves azoimide, detonates at 84°, and is transformed by warming with aniline into *o*-aminosulphonylbenzanilide, m. p. 189°.

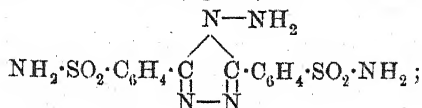
If ethyl *o*-aminosulphonylbenzoate is heated with anhydrous hydrazine at 125° in a closed tube and the product is dissolved in hot water, a triazole derivative crystallises on cooling (see below), and the filtrate from this deposits a substituted hydrazine on acidifying with acetic acid. This compound, 2-hydrazino-1-

benzsulphonazole ("ψ-saccharinhydrazide"), $\text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{N} \cdot \text{C} \cdot \text{NH} \cdot \text{NH}_2$,

crystallises in very long, silky needles, m. p. 257° (decomp.), dissolves in concentrated hydrochloric acid, but not in dilute, is readily soluble in sodium hydroxide, forming a yellow salt, and reduces ammoniacal silver solutions and Fehling's solution at once in the cold. The same compound may be prepared by heating "saccharin" with hydrazine at 125°, or by mixing hydrazine and 2-ethoxy-1-benzsulphonazole (Jesurun, A., 1893, i, 715). The hydrazine derivative yields a *benzoyl* compound, needles, m. p. 276°, a *benzylidene* compound, m. p. 287°, and an *anisylidene* compound, yellow needles, m. p. 270°. With nitrous acid, it reacts to form 2-azido-1-benzsulphonazole, needles, m. p. 153° (vigorous decomp.), which may also be prepared by the action of sodium azide on 2-chloro-1-benzsulphonazole (*ibid.*), and reacts with boiling aniline to form 2-anilino-1-benzsulphonazole,



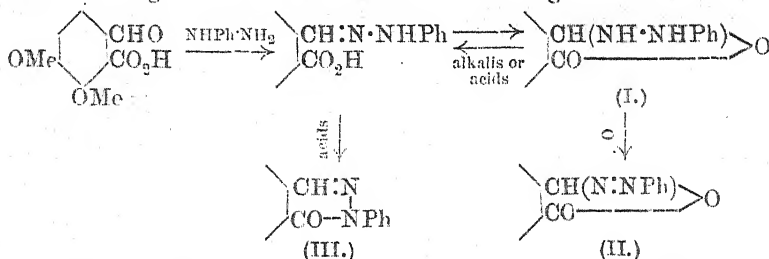
not molten at 300°. The triazole derivative mentioned above is 1-amino-2:5-di-*o*-aminosulphonylphenyl-1:3:4-triazole,



it crystallises in stout, glistening, highly refractive prisms, m. p.

242°, and is soluble without decomposition in the concentrated mineral acids. It forms a 1-benzylideneamino-compound, m. p. 257°; it is converted by the action of concentrated hydrochloric acid at 180° into 1-amino-2:5-di-o-sulphophenyl-1:3:4-triazole, $\text{NH}_2\cdot\text{N}\cdot\text{C}_3\text{N}_2(\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H})_2$, prisms, m. p. above 300°, and it loses the 1-amino-group when treated with nitrous acid, yielding 2:5-di-o-aminosulphonylphenyl-1:3:4-triazole, m. p. 286°. J. C. W.

Action of Phenylhydrazine on Opianic, Nitro-opianic, and Phthalonic Acids. Some Derivatives of Hydrazo- and Azo-phthalide. PRAFULLA CHANDRA MITTER and JNANENDRA NATH SEN (T., 1917, 111, 988—993).—Liebermann (A., 1886, 550) found that opianic and nitro-opianic acids react with phenylhydrazine in the presence of acetic acid to form compounds which are insoluble in alkalis, two molecules of water being eliminated. It is now shown that intermediate, soluble products can be obtained if the free base is applied in ethereal solutions, only one molecule of water being eliminated. The new compounds (I) can be oxidised by mercuric oxide to azo-derivatives of a new type (II), or resolved into Liebermann's compounds (III) by means of acetic acid. The various changes are summarised in the following scheme:



Hydrazo- and azo-compounds of the same types have also been obtained from phthalonic acid, but not in a pure state.

For experimental details, see the original.

J. C. W.

Compounds Derived from Proteins by Energetic Treatment with Nitric Acid. III. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1916, 98, 89—92. Compare A., 1916, i, 512).—Besides the substances previously described, the author has isolated two other compounds from the products of oxidation of various proteins. One of these is succinic acid and the other α -hydroxy- β -methylpropionic acid. The latter acid probably originates from the α -amino- β -methylpropionic acid, which has been shown to be present in caseinogen (compare Foreman, A., 1913, i, 1249).

H. W. B.

Compounds Derived from Proteins by Energetic Treatment with Nitric Acid. IV. *p*-Nitrobenzoic Acid as an Oxidation Product of Proteins. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1916, 98, 93—96. Compare A., 1916, i, 512).—Glutin, which contains phenylalanine, but neither tyrosine nor

tryptophan, yields *p*-nitrobenzoic acid when oxidised with nitric acid. This confirms the conclusion drawn by the author that the *p*-nitrobenzoic acid present among the oxidation products of proteins originates exclusively from phenylalanine.

Phenylalanine has not hitherto been detected as a constituent of (i) keratin from horse's hair, (ii) keratin from goose feathers, (iii) spongin, or (iv) ichthyolepidin. On oxidation with nitric acid, however, all these substances yield a small proportion of *p*-nitrobenzoic acid, and therefore each contains phenylalanine.

H. W. B.

Compounds Derived from Proteins by Energetic Treatment with Nitric Acid. V. Formation of Oxalic Acid from Proteins and Amino-acids. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1916, **98**, 97--115. Compare A., 1916, i, 512).—Glutin and spongin exhibit a marked resistance to nitric acid under conditions in which other proteins are oxidised with formation of 45% of oxalic acid. When fuming acid is employed, oxidation takes place to a certain extent, about 18% of oxalic acid being produced. If, however, about 10% of its weight of cystine, tyrosine, or tryptophan, or a mixture of these amino-acids, is added to glutin, oxidation with ordinary concentrated nitric acid occurs just as with other proteins, and about the usual 45% of oxalic acid is produced. Now glutin does not contain these three particular amino-acids, and, moreover, the removal of these amino-acids from proteins such as fibrin causes the residual amino-acids to become resistant to nitric acid, a resistance which immediately vanishes when one or more of these amino-acids are replaced. Since fuming nitric acid containing free oxides of nitrogen causes oxidation, and it has been shown that cystine, tyrosine, and tryptophan are readily oxidised by nitric acid, with production of oxides of nitrogen, the author draws the conclusion that the presence of these oxides of nitrogen is indispensable for the normal oxidation of proteins with production of the normal quantity (45%) of oxalic acid. The addition of tyrosine, tryptophan, or cystine to spongin likewise ensures its normal oxidation by concentrated nitric acid.

When the nitric acid is allowed to act at 120° instead of at 100°, most amino-acids and proteins are readily oxidised, but only 4--6% of oxalic acid can be recovered from the products of oxidation.

The alleged accelerating action of calcium and magnesium salts in the oxidation of gluten by nitric acid (Sadikoff, A., 1909, i, 750) is not confirmed.

H. W. B.

Comparative Analyses of Fibrin from Different Animals. ROSS AIKEN GORTNER and ALEXANDER J. WUERTZ (*J. Amer. Chem. Soc.*, 1917, **39**, 2239--2242).—Fibrin was prepared from the blood of cattle, sheep, and pigs, and the nitrogen distribution in each sample determined by Van Slyke's method. No differences significantly greater than the probable experimental errors were

found. Thus, apparently, the fibrin from any of these sources can be interchanged in experimental work without vitiating the results.
W. G.

The Crystallisation of Acid Hæmochromogen. CH. DHÉRÉ, L. BAUDOUX, and A. SCHNEIDER (*Compt. rend.*, 1917, **165**, 515—517).—Acid hæmochromogen can be obtained in a crystalline state by heating crystalline hæmin with 60% methyl alcohol and a trace of sodium hyposulphite in a sealed tube at 60—65° for fifteen minutes. At the end of twelve to fourteen hours, acid hæmochromogen is deposited in a crystalline form. The crystals, which are distinctly pleochroic, belong to the rhombic system, the acute angles having a value 84°20'. Complex crystals are sometimes obtained consisting of three simple crystals with their planes perpendicular to one another.
W. G.

[Porphyrins.] Valuation of Spectroscopic Methods. O. SCHUMM (*Zeitsch. physiol. Chem.*, 1916, **98**, 65—72).—Polemical, in reply to Fischer (A., 1916, i. 775), relating to the value to be assigned to spectroscopic methods for the identification of porphyrins and similar compounds.
H W. B.

Constitution of Cotoporphyrin. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1916, **98**, 14—24. Compare A., i, 575, 775).—It has previously been noted that there are two atoms of oxygen in cotoporphyrin which are not in the form of a carboxyl radicle. Apparently, they are not present as alcoholic hydroxyl groups, such as are found in hæmatoporphyrin, because treatment with dilute hydriodic acid in the presence of phosphorus (which readily reduces hæmatoporphyrin to mesoporphyrin) does not effect any reduction of cotoporphyrin. Probably they are combined directly to carbon atoms in the pyrrole nuclei, similarly to those in bilirubic acid. Energetic treatment with hydriodic acid causes disruption of the molecule and liberation of phonopyrrolecarboxylic acid, unaccompanied by any isomeric pyrrolecarboxylic acid or any recognisable basic fraction.

Oxidation of cotoporphyrin with lead peroxide or with chromic acid yields hæmatic acid, which is identical with that obtained from hæmatoporphyrin. On treatment with potassium methoxide under pressure, the molecule is broken down, and among the products are phyllopyrrolecarboxylic acid and a substance, which is possibly a pyrroline derivative.

When methylcotoporphyrin is dissolved in glacial acetic acid and treated with fuming hydrochloric acid and hydrogen peroxide, it is converted into the dihydrochloride of tetrachlorocotoporphyrin, $C_{36}H_{34}O_8N_4Cl_4$, which crystallises in glittering, prismatic needles. The change is accompanied by complete removal of the methyl groups. Corresponding treatment with hydrobromic acid yields the dibromide of tetrabromotrimethylcotoporphyrin, $C_{36}H_{40}O_8N_4Br_6$, glittering needles, in which the methyl groups are retained. These

compounds resemble those obtained from mesoporphyrin (compare Fischer and Röse, A., 1913, i, 1006). H. W. B.

Constitution of Urinoporphyrin. Preparation of a Carboxylated Hæmatic Acid from Urinoporphyrin. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1916, 98, 78—88. Compare A., 1916, i, 575, 775).—When methylurinoporphyrin is dissolved in a mixture of glacial acetic and hydrochloric acids and treated with hydrogen peroxide, a change in colour from red to green rapidly occurs, and, on the addition of water, *tetrachlorotetramethylurinoporphyrin dihydrochloride*, $C_{47}H_{48}O_{16}N_4Cl_6$, is precipitated in radially-marked, little balls. The solution in chloroform examined spectroscopically shows an absorption band in the red and another in the bluish-violet regions of the spectrum. The formation of this tetrachlorourinoporphyrin indicates that the replaceable hydrogen atoms in urinoporphyrin and cotoporphyrin are similarly situated, and are probably contained in α -methine groups, such as are present in the blood pigments. In accordance with this hypothesis, the carboxyl radicles must be in the β -position, and, by oxidation, a *di- β -carboxylated hæmatic acid*, $C_9H_9O_6N$, has actually been obtained. The urinoporphyrin is dissolved in 50% sulphuric acid and treated with chromic acid. The oxidation occurs immediately, and the ether extract yields, on evaporation, prisms, m. p. 180—183°, which, after drying over phosphoric oxide, soften, when heated, at 170°, m. p. 188° (decomp.). The compound is identified by heating in a vacuum, when hæmatic acid is formed, which, at 260°, yields methylethylmaleinimide.

Urino- and coto-porphyrins are readily precipitated from a urine containing porphyrins by the addition of acetic acid. They may be separated by dissolving the mixed porphyrins in methyl alcohol saturated with dry hydrogen chloride, and allowing to remain. After twenty-four hours the crystalline hydrochloride of trimethylurinoporphyrin separates out, from which the urinoporphyrin can be readily regenerated in the manner previously described (*loc. cit.*).

H. W. B.

Influence of Glycerol on the Activity of Invertase. ÉM. BOURQUELOT (*Compt. rend.*, 1917, 165, 567—569).—The activity of invertase, as regards the hydrolysis of sucrose, is weakened by the presence of glycerol, the effect increasing with the proportion of glycerol present. W. G.

Physiological Chemistry.

Amount of Dextrose in Blood. O. SCHUMM (*Zeitsch. physiol. Chem.*, 1916, 98, 179—180. Compare A., 1916, ii, 454).—The author considers that more accurate information regarding the

amount of dextrose in human blood may be obtained by the application of Oppler's "fractional reduction" method (A., 1912, ii, 100).

H. W. B.

Sugar Absorption and the Pancreas. K. VON KÖRÖSY (*Zeitsch. physiol. Chem.*, 1916, **98**, 37—48. Compare A., 1913, i, 1128).—Experiments on dogs are described which indicate that when the blood is prevented from circulating through the organs of the body, including the pancreas, the introduction of a large quantity of dextrose solution into the intestine leads to an increase in the amount of dextrose in the blood; whilst if the pancreas is left in the circulation, under otherwise similar conditions, a decrease in the amount of dextrose in the blood is observed.

H. W. B.

The Normal Metabolism of the Guinea Pig. L. MILLARD SMITH and HOWARD B. LEWIS (*J. Amer. Chem. Soc.*, 1917, **39**, 2231—2239).—Guinea pigs have been fed on a diet of carrots or cabbage, the urine collected in twenty-four hour periods, and determinations made of the total nitrogen, ammonia, carbamide, creatinine, chlorides, and phosphates in the urine and the hydrogen-ion concentration and total acidity of the urine. The creatinine excretion was found to be constant and independent of the nature or extent of the diet, indicating that uniform daily samples of urine were obtained. The creatinine-coefficient was 12 to 14. The hydrogen-ion concentration of the urine was approximately $P_{H+} = 8.9$ on a carrot diet and $P_{H+} = 7.6$ on a cabbage diet, these differences corresponding with the differences in the composition of the ash of these two vegetables. The elimination of total nitrogen was higher on a cabbage than on a carrot diet, the carbamide nitrogen being a constant proportion (84%) of the total nitrogen. The ammonia content of the urine was negligible. The urinary excretion of phosphorus was greater on a carrot than on a cabbage diet.

W. G.

Metabolism of Fats. I. Utilisation of Palmitic Acid, Glyceryl Palmitate, and Ethyl Palmitate by the Dog. J. F. LYMAN (*J. Biol. Chem.*, 1917, **32**, 7—11).—In dogs, 95% of ingested glyceryl palmitate is absorbed. The corresponding figures for ethyl palmitate and palmitic acid are 55% and 32% respectively. Ethyl palmitate is not readily hydrolysed in the alimentary canal, and it is probable, therefore, that the absorption and utilisation of the esters of fatty acids are limited by the rate of hydrolysis. The inferior utilisation of the free palmitic acid is due to disturbance of the digestive processes by the irritating action of the free fatty acid on the digestive organs.

H. W. B.

Metabolism of Fats. II. Effect of Feeding Free Palmitic Acid, Glyceryl Palmitate, and Ethyl Palmitate on the Depot Fat in the White Rat. J. F. LYMAN (*J. Biol. Chem.*, 1917, **32**, 13—16).—The fat deposited in the adipose tissue of rats after feeding with free palmitic acid, glyceryl palmitate, or ethyl palmitate

tate consists chiefly of tripalmitin in all cases. Appreciable amounts of ethyl palmitate or of palmitic acid could not be detected in the adipose tissue during any of the feeding experiments. These results are in harmony with the hypothesis that hydrolysis of fatty substances occurs before absorption, and afterwards the normal fats are synthesised in the tissues.

H. W. B.

Temperature-coefficients of Life Processes. W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1917, **32**, 23—27).—The author points out that life processes consist of a series of consecutive reactions instead of simple chemical reactions (in which the substances formed are not at once broken down), and that change of temperature may affect the former in an entirely different manner from that in which it affects the latter. It is shown, by examples, that in the case of consecutive reactions, if the reaction in which a substance is formed has a different temperature-coefficient from that in which it is destroyed, the type of curve showing the rate of disappearance of the substance may be completely altered by a change in the temperature. Caution must therefore be exercised in interpreting the temperature-coefficients of consecutive reactions, to which category many life processes undoubtedly belong.

H. W. B.

Hæmatoporphyrin congenita and the Natural Porphyrins. O. SCHUMM (*Zeitsch. physiol. Chem.*, 1916, **98**, 123—178).—In hæmatoporphyrin congenita, the blood contains free hæmatin and a porphyrin. On the addition of acetic acid to the urine, the porphyrin is precipitated, and on spectroscopic examination is found closely to resemble urinoporphyrin (compare Fischer, A., 1916, i, 514; this vol., i, 713). The urine usually contains about 0.02% of porphyrin, whilst the quantity passed daily varies between 0.3 and 0.4 gram.

Comparison of the absorption spectra of urinoporphyrin, coto-porphyrin, hæmatoporphyrin, and mesoporphyrin reveals small differences which indicate that all these porphyrins are distinct compounds.

H. W. B.

Porphyrin Occurring in Urine after Trional-poisoning. ALEXANDER ELLINGER and OTTO RIESSER (*Zeitsch. physiol. Chem.*, 1916, **98**, 1—10).—The porphyrin present in the urine after trional poisoning is apparently identical with that discovered by Hans Fischer (A., 1915, i, 514; see also this vol., i, 713) in the urine in a case of congenital hæmatoporphyrinuria, and termed by him urinoporphyrin. It gives the same analytical and spectroscopical data, and shows the same chemical and biological behaviour as urinoporphyrin; the only point of difference observed is in the melting point of the methyl ester, which is found to be 255—257° instead of 290° given by Fischer. The reason for this observed difference could not be discovered.

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Production of Cholesterol Esters in Fatty Degeneration. FRANZ VALENTIN (*Zeitsch. physiol. Chem.*, 1916, **98**, 73—77).—A portion of degenerated adipose tissue from a pig was observed under

amount of dextrose in human blood may be obtained by the application of Oppler's "fractional reduction" method (A., 1912, ii, 100).

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Production of Cholesterol Esters in Fatty Degeneration. FRANZ VALENTIN (*Zeitsch. physiol. Chem.*, 1916, **98**, 73—77).—A portion of degenerated adipose tissue from a pig was observed under

the microscope to contain numerous crystals of two distinct types. Extraction with ether yielded considerable quantities of the fatty acid esters of cholesterol and of free fatty acids; the presence of a lipase in the adipose tissue was also demonstrated. The author suggests that the free fatty acids present in the specimen of adipose tissue represent the products of the action of the lipolytic enzyme, whilst the cholesterol esters have been subsequently synthesised directly from the free acids and cholesterol. H. W. B.

Human Gall Stones. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1916—1917, **98**, 25—36, 281—284).—Human gall stones contain free palmitic acid and a bile acid, which is probably deoxycholic acid.

When a solution of cholesterol in warm butyric acid is cooled, needle crystals appear, which consist of *cholesterol butyrate*. The compound is very easily hydrolysed; on treatment with alcohol, free cholesterol is regenerated. H. W. B.

Behaviour of Dimethylenegluconic Acid and Methylene-saccharic Acid in the Organism. CESARE PADERI (*Arch. Farmacol. sperim.*, 1917, **23**, 353—370; from *Chem. Zentr.*, 1917, ii, 239).—Both acids in the form of their sodium salts are readily tolerated by rabbits. Formaldehyde is not present in the urine which contains the unchanged acids, which must therefore be very stable in the organism. This behaviour is in striking contrast with that of anhydromethylenecitric acid, which is readily hydrolysed with the formation of formaldehyde. The difference is probably due to the fact that, in the former acids, the hydrogen atoms of the methylene group are replaced by two alcoholic hydroxyl groups, whilst in the latter the carboxyl group is also affected. H. W.

Combustion of Benzene in the Human Organism. DIONYS FUCHS and ALADÁR VON SOÓS (*Zeitsch. physiol. Chem.*, 1916, **98**, 11—13).—The administration of 71 grams of benzene to a man suffering from leucæmia was followed by the elimination of muconic acid in the urine, 0.08 gram of the pure substance being isolated. The oxidation of the benzene nucleus according to the equation $C_6H_6 + 2O_2 = CO_2H \cdot CH : CH \cdot CH : CH \cdot CO_2H$, occurs, therefore, in man as well as in rabbits and dogs (compare Jaffé, A., 1909, ii, 914). H. W. B.

Toxicity of Aromatic Nitro-compounds. F. KOELSCH (*Münch. med. Woch.*, 1917, **64**, 965—968; from *Chem. Zentr.*, 1917, ii, 309).—The aromatic nitro-compounds have previously been classed in the literature as a group possessing equal toxicity and similar physiological properties. The author gives a series of results obtained by experiments on animals, together with data obtained from the munition industry, and discusses the injury to the health of the workers and the necessary precautions. The following substances are considered: the nitrated benzenes, toluenes, and xylenes, nitronaphthalenes, trinitrotoluene, and the nitrated phenols. The original paper must be consulted for details. H. W.

Pharmacological Studies of the Ipecacuanha Alkaloids and some Synthetic Derivatives of Cephaeline. II. Emetic Effect and Irritant Action. A. L. WALTERS, C. R. ECKLER, and E. W. KOCH (*J. Pharm. Exper. Ther.*, 1917, 10, 185—197. Compare Walters and Koch, this vol., i, 612).—In cats, the emetic dose of emetine hydrochloride is approximately twice that of cephaeline hydrochloride, and the higher homologues of the series decrease in emetic power very much in the same ratio as they do in toxicity (*loc. cit.*). The hydrochloride, hydrobromide, and hydriodide of emetine possess about equal emetic power, but the hydriodide of cephaeline *isoamyl* ether, owing to its relative insolubility, is about one-half as emetic as the hydrobromide or hydrochloride of cephaeline *isoamyl* ether, and only one-sixth as emetic as emetine hydrochloride.

When tested on the conjunctiva of rabbits, emetine and cephaeline are the most irritant, and cephaeline *isoamyl* ether is the least irritant of the series. When injected intramuscularly in rabbits, cephaeline *isoamyl* ether is the most irritant, whilst the difference between the other less irritant members of the series is not marked. In man, the hypodermic injection of cephaeline *isoamyl* ether phosphate or hydrochloride causes severe pain, soreness, and local inflammation, whilst with the corresponding propyl ether phosphate, only a slight local reaction is noticeable.

H. W. B.

Fate of Caseinogen after Intravenous Injection. B. VON AARON (*Zeitsch. physiol. Chem.*, 1916, 98, 49—58).—About 58% of the caseinogen administered intravenously to dogs passes unchanged into the urine.

H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

The Effects of Alkali Salts on Nitrification. P. E. BROWN and E. B. HIRONCKO (*Soil Sci.*, 1917, 4, 207—229).—A study of the effect of applications of sodium chloride, sodium sulphate, magnesium sulphate, and calcium carbonate to normal soil, and of sodium hydrogen carbonate, sodium carbonate, calcium carbonate, and calcium sulphate to an alkali soil, on nitrification in the soil. In the first group, it was found that the toxicity varied with the soil. In the particular soil studied, sodium chloride had a toxic effect at a concentration of 0.02%, sodium sulphate at 2.0%, and calcium carbonate at a point between 1.5 and 6.0%. In the second group, calcium sulphate had no effect, calcium carbonate acted as in the normal soil, whilst sodium carbonate and sodium hydrogen carbonate both had a toxic effect at a concentration of 0.30%. Similar tests in greenhouse soils agreed with these laboratory tests

for alkali soils. In the normal soils, however, in the greenhouse tests the sodium sulphate had a toxic effect at a concentration of 0.5%. The effect of the salts on crop growth was similar to that on nitrification.

W. G.

The Nature of Ammonification. K. MIYAKE (*Soil Sci.*, 1917, 4, 321—325).—A further study of the ammonification of leucine and tyrosine in five different types of soils confirms the statement that this process is an autocatalytic chemical reaction (compare this vol., i, 244). In the case of the two compounds mentioned, it was found that the whole of the nitrogen added was not transformed into ammonia during the process, and that the amount so transformed varied with the nature of the compound added and of the soil to which it was applied.

W. G.

Chemistry of Nutrition. TH. BOKORNY (*Arch. Anat. Physiol. Physiol. Abt.*, 1916, 255—294; from *Chem. Zentr.*, 1917, ii, 232).—The number of organic substances which can serve as nutriment for green plants is large and includes the following compounds: For fungi: methyl, ethyl, and propyl alcohols; phenol, glycerol, ethylene glycol, erythritol, mannitol, dulcitol, quinol, tannin, formic, acetic, oxalic, propionic, lactic, succinic, tartaric, butyric, citric, aspartic, glyoxylic, pyruvic, lævulic, salicylic, quinic, benzoic, fumaric, malonic, and malic acids; sucrose, dextrose, lævulose, galactose, lactose, rhamnose, sorbinose, arabinose, maltose, inositol, mannose, xylose, erythrodestrin, salicin, amygdalin, raffinose, dextrin, inulin, cellulose nitrate, cellulose, *p*-hydroxybenzaldehyde, carbamide, glycine, trimethylamine (?), methylamine, propylamine, asparagine, aspartic acid, leucine, tyrosine, toluidine, aniline, creatine, hydantoin, allantoin, peptone, acetoacetic ester, acetone, formaldehyde as methylal, or, less frequently, as sodium formaldehyde sulphite, acetaldehyde, *p*-hydroxybenzaldehyde. For algae and other green plants: methyl alcohol, ethyl alcohol (?), phenol, glycerol, ethylene glycol, mannitol, dulcitol, acetic, oxalic, propionic, lactic, succinic, tartaric, butyric, valeric, citric, aspartic, glyoxylic and malic acids, sucrose, dextrose, lævulose, galactose, lactose, maltose, formaldehyde, carbamide, glycine, trimethylamine, aspartic acid, leucine, tyrosine, creatine, hydantoin, formaldehyde (free and as methylal or sodium formaldehyde sulphite), peptone, acetoacetic ester. For the full details the original paper must be consulted.

H. W.

Action of Radium on Plants in Water Cultures. FERDINAND PILZ (*Zeitsch. Landw. Versuchswesen Oesterreich*, 1916, 399; from *Bied. Zentr.*, 1917, 46, 412—414).—Experiments were made with the crude residues from the extraction of uranium ore, the radium content of the former being 0.4 mg. per kilo. The material was diluted one hundred times by admixture with pure quartz sand before being employed for the water cultures. Peas and maize were grown in Tollens's solution, which was changed weekly, with the addition of 1 gram of the radium mixture in the earlier stages and

2 grams in the later ones. Thus the set of plants in each culture vessel received 29 grams of the mixture or 0.000116 mg. of radium during the vegetation period. The results show a marked response of the pea plants to the presence of radium, the total dry matter being increased by 28 per cent., whilst the number of pods was increased by 43 per cent. With maize the effect was less pronounced; the total dry matter of the treated plants was 15% higher, but the yield of grain was decreased by 47 per cent. This is attributed to the effect radium has on the retardation of ripening.

Analyses of the plants showed that the percentage of nitrogen, phosphoric acid, potassium, and calcium in the plants grown in the presence of radium is lower than in the controls. The calcium content of the roots is especially reduced, and this effect of decreasing calcification of the root vessels is held to be analogous to the effect of radium on the animal organism.

H. B. H.

Seeds of *Pangium Edule* and of *Hydnocarpus Alcalæ*.
HARVEY C. BRILL (*Philippine J. Sci.*, 1917, 12, [A], 37—46).—The seeds of *Pangium edule*, a plant found in various parts of the Philippine Islands, are about 5 cm. long by 3 cm. wide, and are embedded in a crustaceous pericarp which is about 22 cm. long by 15 cm. in diameter. They contain a cyanogenetic glucoside, which is identical with gynocardin isolated from *Gynocardia odorata* and the leaves of *Pangium edule* (compare Power, Lees, and Barrowcliff, T., 1905, 87, 349, 896; De Jong, A., 1909, ii, 424); an enzyme, gynocardase, is also present. The quantity of oil in the dry kernels is 21%. The fruit of *Hydnocarpus alcalæ* resembles a small, unhusked coconut and contains numerous seeds about 4 cm. long; the seeds yield 65% of oil. The presence of a cyanogenetic glucoside is doubtful. The two oils have the following physical and chemical characters:

	<i>Pangium edule</i> .	<i>Hydnocarpus alcalæ</i> .
M. p.	About 2°.	32°.
D ₂₀	0.9049	0.9502
[α] _D in chloroform	+4.28°	+49.60°
n _D	1.4665	1.4770
Iodine number	113.1	93.1
Saponification number.....	190.3	188.9
Reichert-Meißl number	—	4.43

The oil from *Pangium edule* seeds contains a small quantity of an optically active acid (hydnocarpic or chaulmoogric acid), whilst the oil from *Hydnocarpus alcalæ* seeds contains chaulmoogric acid, but not hydnocarpic acid.

W. P. S.

Methods for Approximating the Relative Toxicity of Cotton-seed Products. FRANK E. CARRUTH (*J. Biol. Chem.*, 1917, 32, 87—90).—During the expression of the oil from partly cooked cotton-seed by the hot pressing process, the glands containing the gossypol are disintegrated and the gossypol is spread over the surface of the seed tissue. Apparently, in these circumstances, the

gossypol undergoes oxidation, and is transformed into "D" gossypol, which is much less toxic and less soluble than ordinary gossypol. The toxicity of cotton-seed products is due chiefly to the presence of unchanged gossypol, which may be detected in the following ways: (1) a portion of the meal is sprinkled on a glass slide and touched with a drop of concentrated sulphuric acid. The result is observed immediately through the low power of a microscope. In the presence of unchanged gossypol, numerous red areas appear where the acid touches the more or less disintegrated glands; (ii) about 200 grams of the meal are extracted with ether. The extract is concentrated, filtered, and treated with about one-tenth of its weight of aniline. After warming on the water-bath, the mixture is left for several days. The more gossypol there is present, the quicker will be the appearance of a yellow, microcrystalline precipitate of the *dianiline* salt of gossypol, $C_{30}H_{28}O_9 \cdot 2C_6H_5 \cdot NH_2$, which can be collected on a tared Gooch crucible, washed with ether and light petroleum, dried at 100° , and weighed.

Cotton-seed meal which has been cooked for twenty to thirty minutes during the pressing process may be practically free from toxic properties, and the ethereal extract treated in the manner described above fails to give any precipitate with aniline.

The meal prepared by the cold pressing process may not be more toxic than the hot pressed meal. It appears that most of the gossypol passes in the former process into the oil, from whence it is subsequently entirely removed during the process of refining.

H. W. B.

[**Oxalic Acid in Foods.**] E. ARBERG (*Mitt. Lebensmittelunters. Hygiene*, 8, 98—104; from *Chem. Zentr.*, 1917, ii, 320—321).—See this vol., ii, 583.

Occurrence of Manganese in Insect Flowers and Insect Flower Stems. C. C. McDONNELL and R. C. ROARK (*J. Agric. Research*, 1917, 11, 77—82).—The authors have determined the amounts of manganese present in the stems, "open" flowers, and "closed" flowers of *Chrysanthemum cinerarioides* from Japan and from Dalmatia, and find that the manganese content of both stems and flowers vary considerably and is but little different in the two parts of the plant. The estimation of the manganese content of an insect powder in order to detect adulteration with powdered stems is therefore useless. Pyrethrum of Japanese origin contains more manganese than that from other countries, probably owing to the high manganese content of the volcanic soils of Japan. The manganese, nitrogen, and phosphoric acid content of pyrethrum vary in the same direction.

W. G.

The Diastatic Degradation of Inulin in Chicory Root. J. WOLFF and B. GESLIN (*Compt. rend.*, 1917, 165, 651—653).—Inulin breaks down in the chicory root under the influence of enzyme action to levulose with the intermediate formation of compounds which the authors call inulides, these being capable of con-

version into l  vulose by the hydrolytic action of the juice itself. They are also fermented by different yeasts, but vary in their resistance to this action. The fresh juice of the chicory, although capable of hydrolysing these inulides, is without action on pure inulin.

W. G.

Preparation of Durable Fruit Extracts, which contain the Fragrant Substances and Enzymes of the Fruit Juices in an Undecomposed Form. H. THOMS (*Ber.*, 1917, 50, 1240—1242; D.R.-P., 285304, June, 1914).—The fruit juices are dialysed (for apparatus, see this vol., ii, 561), and so freed from most of their dissolved acids, and then evaporated to syrups in vacuum pans at below 40  . The extracts thus contain the undecomposed enzymes, but are durable. A pineapple syrup is described which contained about 3.5% of valuable proteolytic enzymes.

J. C. W.

Effect of Three Annual Applications of Boron on Wheat. F. C. COOK and J. B. WILSON (*J. Agric. Research*, 1917, 10, 591—597).—The boron was used in the form of borax or colemanite as a fly larvicide for horse manure, which was then applied to the soil. Four plots were used: (1) unmanured, (2) manured control, (3) manured plus borax, (4) manured plus colemanite. The amount of borax applied in the first year was equivalent to 0.0088% boric acid to the top 0.15 metre of soil and 0.0022% in the two subsequent years. The amount of colemanite applied was equivalent to 0.0029% boric acid to the top 0.15 metre of soil each year. In the first two years the borax reduced the yield of grain by 10% against the manured control, while the colemanite had little, if any, effect. In the last year, when the yields from all four plots were low and the proportion of straw to grain was high, the borax plot gave the best yield. Only minute amounts of boron were absorbed by any of the wheat plants, and in all cases a relatively uniform distribution of boron in the straw and grain was found. Only in the first year on the borax plot was a yellowing of the plants observed, and a sample of soil from this plot taken nine months later showed the presence of boron soluble in weak acid. In no other soil sample was any soluble boron found. There was no evidence of any cumulative action of boron in the soil. W. G.

The Occurrence of *l*-Leucine in Sweet Clover Silage. G. P. PLAISANCE (*J. Amer. Chem. Soc.*, 1917, 39, 2087—2088).—Although mannitol is readily isolated from silage made from maize, cane and sunflower (Dox and Plaisance, this vol., i, 683), sweet clover silage yields no trace of mannitol, but extraction with alcohol in this case yields *l*-leucine in quantity corresponding with 0.4 to 1% of the dry material. No sample of maize silage has been found to contain *l*-leucine.

D. F. T.

Effect of Paraffin on the Accumulation of Ammonia and Nitrates in the Soil. P. L. GAINES (*J. Agric. Research*, 1917, 10, 355—364).—The unsatisfactory results obtained by the "paraffin

wire-basket method" of studying soil fertility (compare Gardner, U.S. Dept. Agric. Bur. Soils, Circ. 18) are shown to be due to the growth of certain saprophytic fungi, which is encouraged by the paraffin either in the form of wax or oil. This development of fungi is accompanied by the disappearance of active ammonia or nitrate nitrogen. Very similar results are obtained whether the bottle containing the soil is simply coated on the inside with paraffin wax, or chips of the wax or paraffin oil are incorporated with the soil. When nitrogen is added to the soil in the form of cotton-seed meal, vigorous ammonia and nitrate formation occurs, but the nitrogen in these two forms rapidly disappears owing to the action of the fungi. W. G.

Some Factors Affecting Nitrate-Nitrogen Accumulation in Soil. P. L. GAINES and L. F. METZLER (*J. Agric. Research*, 1917, 11, 43—64).—A study of the effects of varying the depth of the column of soil, its moisture content, and compactness on nitrate accumulation. The experiments were carried out in the laboratory on a silt loam. The results indicate that as the moisture content of a soil decreases, increasing the compactness from a very loose condition will increase the accumulation of nitrate nitrogen. The optimum moisture content for any degree of compactness is such that the soil contains about two-thirds of the total amount of moisture it will retain. When this condition is fulfilled, aeration will be sufficient to the depth of 3 decimetres with any degree of compactness, and it is further found that the accumulation of nitrate nitrogen increases with increasing depth down to 6 decimetres. Nitrate nitrogen accumulates more rapidly in unbroken soil columns than in artificial columns of powdered, sieved soil. Aeration in a column of soil uncultivated for seven years was found to be far in excess of that required to maintain aerobic conditions. W. G.

Absorption and Nitrification of Ammonium Compounds in the Presence of Zeolites in Soil. Estimation of Ammonia in Soil and on Zeolithic Substances. F. MÜNTER (*Landw. Versuchs. Stat.*, 1917, 90, 147—189).—Sandy soil possesses an appreciable capacity of absorbing ammonia from ammonium sulphate. A portion of this absorbed ammonia can be recovered by distillation with magnesia, but upwards of 10% is more firmly retained. By the addition of zeolites, the amount absorbed may be increased by a further 20—25% of the total added. It is found that the ammonia held by sandy soil is more easily nitrified than that held by zeolites. Soil and zeolite react similarly in retaining some ammonia when boiled with magnesia, but whilst that held by the latter can be completely recovered by a further addition of potassium chloride before distillation, some of that retained by the soil is much more resistant to treatment. Pure sand is unable to absorb ammonia, and the addition of silicic acid and aluminium hydroxide is without effect.

Experiments were made on the estimation of ammonia in soils,

and the result obtained that the hydroxides and carbonates of calcium, barium, strontium, and sodium, with or without the addition of neutral salts, either fail to expel all the absorbed ammonia or else lead to decomposition of the soil organic matter. The general conclusion is drawn that adsorption and absorption occur simultaneously in the soil without any definite relation existing between the two.

H. B. H.

An Agronomic Study of several Fertilising or Anticryptogamic Compounds Used in Agriculture. BOGUMIL DE WILKOSZEWSKI (*Arch. Sci. phys. nat.*, 1917, [iv], 44, 165—189, 256—275).—Solutions of various salts have been allowed to percolate through columns of natural and artificial soils of different types and the water draining through examined. Iron in solution as ferric sulphate is more rapidly absorbed by the soil than in the ferrous state, any iron retained from ferrous sulphate being found in the ferric state in the soil. The salts are converted into their hydroxides, the ferrous hydroxide being subsequently oxidised and held in the soil in the ferric state. This hydrolysis is markedly favoured by the presence of the soil particles. Similar results were obtained with manganese sulphate and copper sulphate, the salt in all cases undergoing hydrolysis, and, where possible, oxidation, the base being retained in the soil and the acid ion passing on into the drainage water.

In the case of calcium cyanamide, this material is converted into carbamide, ammonium carbonate, and subsequently calcium nitrite and nitrate, the reaction being much more rapid where a solution is used than when the solid is itself mixed into the soil. The author considers that micro-organisms are not essential for these changes, as they occurred in a sterilised soil. The oxidation to nitrite and nitrate goes on most rapidly in soils of a porous nature, such as the infusorial earths. The author finds that, in the presence of calcium cyanamide, Nessler's reagent does not give the red precipitate with ammonium salts.

W. G.

The Divergent Effects of Lime and Magnesia on the Conservation of Soil Sulphur. W. H. MACINTYRE, L. G. WILLIS, and W. A. HOLDING (*Soil Sci.*, 1917, 4, 231—237).—Calcium oxide, magnesium oxide, precipitated calcium carbonate, precipitated magnesium carbonate, ground limestone, ground dolomite, and ground magnesite respectively were mixed in with a sandy loam at rates corresponding with 19, 79, and 247 tonnes of calcium oxide per hectare. The samples of soil were then placed in lysimeters either directly on a sand filter bed or having an intermediate 0.3 metre of clay subsoil. The soils were leached by rain and the total alkalinity of, and sulphur in the drainage waters, for two successive years determined. The interposition of the subsoil checked the loss of sulphur by drainage except in the second year after the application of magnesium oxide and magnesium carbonate. The 19-tonne application of calcium oxide slightly depressed the

sulphur in the drainage waters as compared with the other equivalent dressings, but the 79-tonne and 247-tonne treatments practically inhibited the outward movement of sulphur in solution. All the natural carbonates appeared to bring about conditions causing an increased washing out of sulphur as compared with subsoil tanks receiving no application of carbonate. W. G.

Formation of "Black Alkali" (Sodium Carbonate) in Calcareous Soils. J. F. BREAZEALE (*J. Agric. Research*, 1917, 10, 541—590).—The formation of sodium carbonate by the action of calcium carbonate on aqueous solutions of sodium nitrate, chloride, or sulphate may be checked, and even prevented, by the presence of relatively small amounts of calcium nitrate or chloride, but a saturated solution of calcium sulphate does not entirely stop the formation of sodium carbonate. In the presence of carbon dioxide, it is sodium hydrogen carbonate which is formed, and the soluble calcium salts have the same effects as in the first case. Thus a field application of gypsum will not overcome "black alkali" if the soil or the irrigation water contains soluble sulphates in appreciable amounts, this formation of sodium carbonate in the soil by interaction of the calcium carbonate and sodium salts proceeding as in aqueous solutions. The sodium carbonate thus formed decomposes the organic matter of the soil, giving very toxic compounds, which may be the cause of the barren or "slick" spots in calcareous soils. The decomposition of the organic matter by the sodium carbonate is checked to some extent by the presence of sodium chloride or sodium sulphate.

A calcareous hardpan may produce "black alkali" by interaction with soluble sodium salts washed down from the upper layers of the soil or brought up from below in the soil water by capillary action. W. G.

The Isolation from Peat of certain Nucleic Acid Derivatives. W. B. BOTTOMLEY (*Proc. Roy. Soc.*, 1917, [B], 90, 39—44).—Extraction of air-dried, raw peat with a 1% solution of sodium hydrogen carbonate, the extract being filtered, neutralised with hydrochloric acid, concentrated in a vacuum to a small volume, and then poured into alcohol containing sodium acetate and hydrochloric acid, did not give nucleic acid. The precipitate when examined by Jones's method of hydrolysis was found to contain the dinucleotide, adenine-uracil-dinucleotide, whilst the filtrate contained phosphoric acid, sugar, guanine, and cytosine, the four radicles of a guanine-cytosine-dinucleotide. The nucleic acid in peat is thus apparently split up during peat formation in the same manner as that found for yeast-nucleic acid by Jones and Germann (compare A., 1916, i, 515). W. G.



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